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⑭ 発明の名称 電子写真感光体

⑰ 特 願 昭63-266720

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## 明 細 書

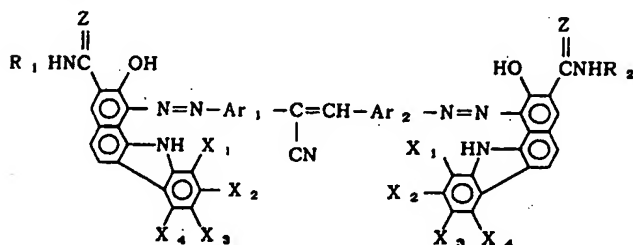
## 1. 発明の名称

電子写真感光体

## 2. 特許請求の範囲

(1) 導電性支持体上に電荷発生層と電荷輸送層を有する積層型電子写真感光体において、電荷発生層は電荷発生物質として、

一般式(1)

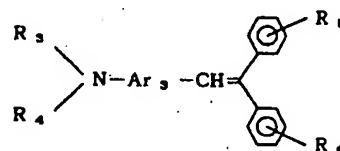


(式中、R<sub>1</sub> および R<sub>2</sub> はアルキル基、アラルキル基、芳香環基、または複素環基を示し、Ar<sub>1</sub> および Ar<sub>2</sub> は芳香環基または複素環基を示し、X<sub>1</sub>、X<sub>2</sub>、X<sub>3</sub> および X<sub>4</sub> は水素原子、アルキル基、アルコキシ基、ハロゲン原子、ニ

トロ基、シアノ基またはトリフルオロメチル基を示し全てが水素原子であることはない。Z は酸素原子又は硫黄原子を示す。)

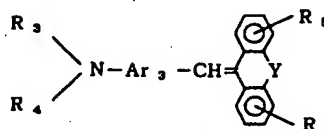
で示されるジスアゾ顔料を含有し、電荷輸送層は電荷輸送物質として、

一般式(2)



あるいは

一般式(3)



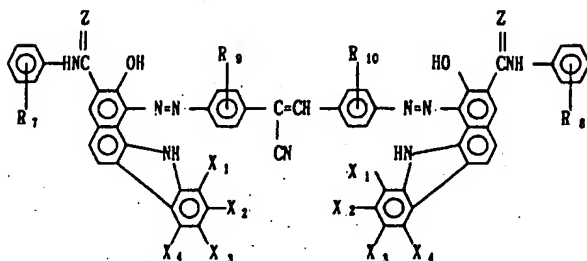
(式中、R<sub>3</sub> および R<sub>4</sub> はアルキル基、アラルキル基、芳香環基または複素環基を示し、R<sub>5</sub> および R<sub>6</sub> は水素原子、アルキル基、アルコキシ基またはハロゲン原子を示し、Ar<sub>3</sub> は

芳香環基または複素環基を示す。Yは単結合、  
 $-\text{CH}_2-\text{CH}_2-$ または $-\text{CH}=\text{CH}-$ を示す。)

で示されるスチリル化合物を含有することを特徴とする電子写真感光体。

## (2) 電荷発生物質は

一般式(4)



(式中、 $R_7$  および  $R_8$  は水素原子、アルキル基、アラルキル基、芳香環基、アルコキシ基、ハロゲン原子、ニトロ基、シアノ基またはトリフルオロメチル基を示し、 $R_9$  および  $R_{10}$  は水素原子、アルキル基、アラルキル基、芳香環基、アルコキシ基、ハロゲン原子、シアノ基またはトリフルオロメチル基を示す。 $Z$ 、

一方、電荷発生機能と電荷輸送機能とをそれぞれ別個の物質に分担させた機能分離型電子写真感光体が、従来の有機感光体の欠点とされていた感度や耐久性に著しい改善をもたらした。このような機能分離型感光体は、電荷発生物質、電荷輸送物質の各々の材料選択範囲が広く、任意の特性を有する電子写真感光体を比較的容易に作製し得るという利点を有している。特に電子写真感光体が複写機のみならず、近年ではレーザービームプリンター、LEDプリンター等に用いられるようになるにつれ、使用する光源の発光波長に合った分光感度域を設定するためには機能分離型が適している。

電荷発生物質としては、種々のアゾ顔料、フタロシアニン顔料、多環キノロン顔料、シアニン色素スクエアリツク酸染料、ビリリウム塩系色素等が知られている。中でもアゾ顔料は耐光性が強い、電荷発生能力が大きい、材料合成が容易等の点から多くの構造が提唱されてきた。例えば本発明に類似のジスアゾ顔料として特開昭56-116040号公報、特開昭57-182747号公報、特開昭58-49952

$X_1$ 、 $X_2$ 、 $X_3$  および  $X_4$  は一般式(1)と同じ意味を示す。)

で示されるジスアゾ顔料である特許請求の範囲第1項記載の電子写真感光体。

## 3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は電子写真感光体に関し、詳しくは電荷発生物質を含有する電荷発生層と、電荷発生物質が発生したキャリアを受けとり、これを搬送する電荷輸送物質を含有する電荷輸送層を有する積層型電子写真感光体に関する。

〔従来技術〕

このような有機感光体としては、ポリ-N-ビニルカルバゾールに代表される光導電性ポリマー及びこれと2,4,7-トリニトロ-9-フルオレノン等のルイス酸とから形成される電荷移動錯体を主成分とする感光層を有する電子写真感光体はすでに実用化されている。しかし、この感光体は、感度および耐久性において必ずしも満足できるものではない。

号公報、特開昭58-115447号公報、特開昭59-72448号公報、特開昭59-155848号公報、特開昭58-115446号公報、特開昭58-115446号公報、特開昭59-7366号公報等がすでに公知である。ここで電荷発生物質として用いられるアゾ顔料に要求されることは(i)熱・光に対して安定であること、(ii)分離状態で電荷発生能を示すものでは、分散が容易であること及び分散液の経時変化の少ないこと、(iii)電荷発生能が温度により変化しないこと、(iv)繰り返し使用時において特性の変化のないこと、(v)用いる光源に対して有効な分光感度域をもっていること、(vi)電荷輸送物質が限定されないこと等があげられる。これらの要求を高いレベルで平均的に満足することが実用上最も重要なことである。前述の公知顔料の中には上記要求の一部は満足するもののすべてを高いレベルで満足するものはなかった。

一方、電荷輸送物質としては、ヒドラゾン化合物、ピラズリン化合物、スチルベン化合物、トリアルールメタン化合物、アリールアミン化合物等

が知られている。これらの化合物に要求されることは (i) 光・熱に対して安定であること、(ii) コロナ放電により発生するオゾン、 $\text{NO}_x$ 、硝酸等に対して安定であること、(iii) 高い輸送能を示すこと、(iv) 有機溶剤結着剤との相溶性が高いこと等があげられる。

前述の公知アゾ顔料と電荷輸送物質との組合せとしては例えば、特開昭58-18636号公報、特開昭57-204551号公報、特開昭59-44050号公報、特開昭59-44051号公報、特開昭59-157644号公報、特開昭60-24549号公報、特開昭60-24550号公報、特開昭60-24551号公報、特開昭60-24552号公報等があげられる。

これらの組合せによる感光体は、繰返し使用時における電位変動は少ないものの、使用環境の変化による画像の劣化がみられる等、画像特性上大きな欠点を有するものが多く、実際の使用上問題となっている。

〔発明が解決しようとする問題点〕

本発明の目的は、電荷発生層と電荷輸送層とを

有する機能分離型感光体において、大きな感度を有し、しかも繰返し使用時の電位が安定に維持され、かつ使用環境（温度、湿度）によらず安定した感度と画像特性を示すことのできる電子写真感光体を提供することである。

また、本発明の目的は、アゾ顔料の分散が容易でしかも分散液の経時変化の少ないアゾ顔料を提供することである。

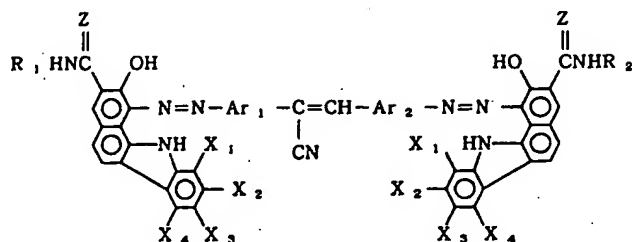
また、本発明の目的は、600から700nmの領域の光源に対して、十分大きな感度を示す電子写真感光体を提供することである。

また、本発明の目的は、コロナ放電により発生するオゾン、 $\text{NO}_x$ 、硝酸等に対して安定な感光体を提供することにある。

〔問題点を解決するための手段〕

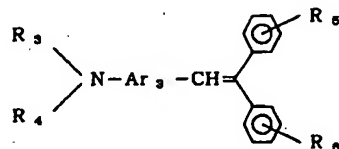
本発明者らの検討の結果、特定構造のジスアゾ顔料を含有する電荷発生層と特定構造のスチリル化合物を含有する電荷輸送層とを有する積層型電子写真感光体が、前記問題点を解決し優れた電子写真特性を示すことを見出した。

すなわち本発明は、導電性支持体上に電荷発生層と電荷輸送層を有する積層型電子写真感光体において、電荷発生層は電荷発生物質として、一般式(1)



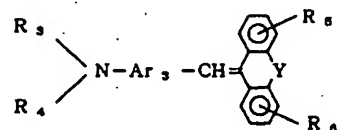
で示されるジスアゾ顔料を含有し、電荷輸送層は電荷輸送物質として、

一般式(2)



あるいは

一般式(3)



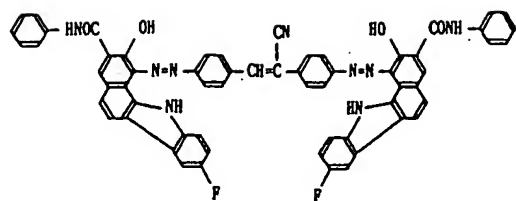
で示されるスチリル化合物を含有することを特徴とする電子写真感光体である。

一般式(1)中、 $R_1$  および  $R_2$  は、アルキル基、アラルキル基、芳香環基または複素環基を示し、具体的にはメチル、エチル、プロピル、ブチル等のアルキル基、ベンジル、フェネチル、ナフチルメチル等のアラルキル基、フェニル、ジフェニル、ナフチル、アンスリル等の芳香環基および、カルバゾール、ジベンゾフラン、ベンズイミダゾロン、ベンズチアゾール、チアゾール、ピリジン等の複素環基が挙げられる。

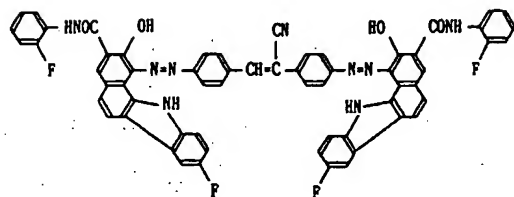
また、これらのアルキル基、アラルキル基、アリール基、芳香環基および複素環基は例えばメチル、エチル、プロピル等のアルキル基、またはメトキシ、エトキシ、プロポキシ等のアルコキシ基、



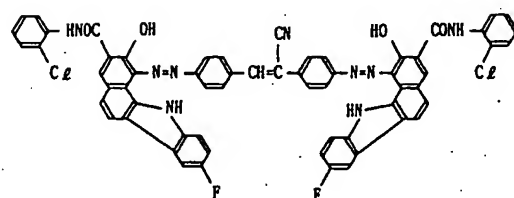
G-1



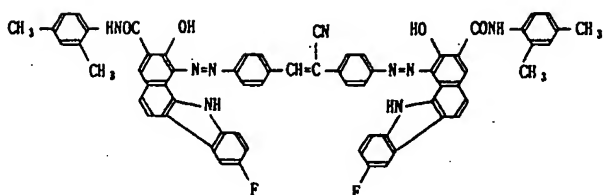
G-2



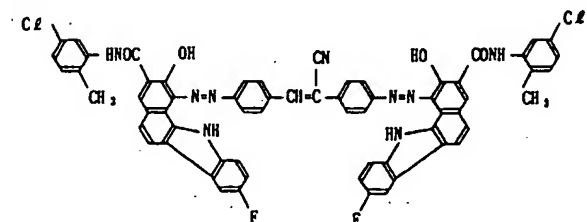
G-3



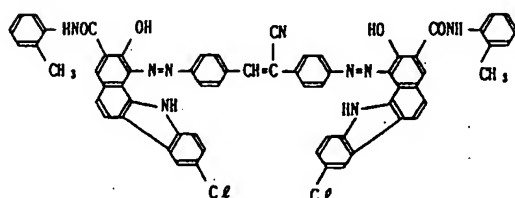
G-7



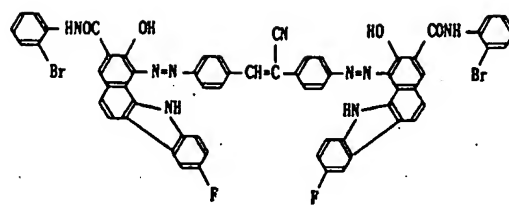
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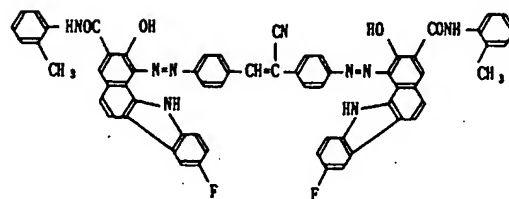
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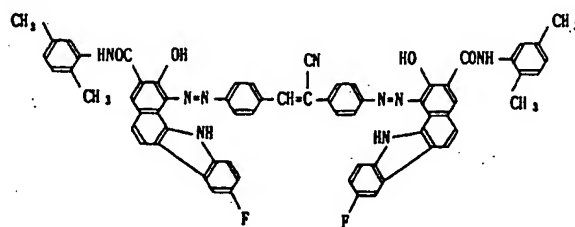
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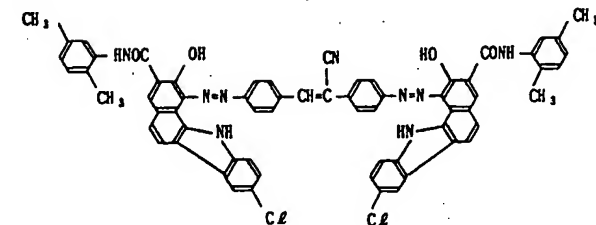
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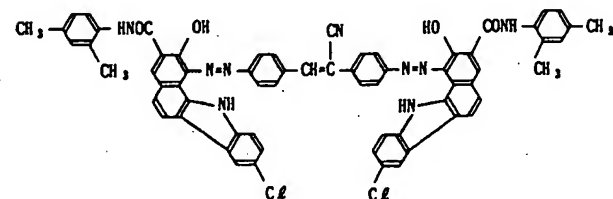
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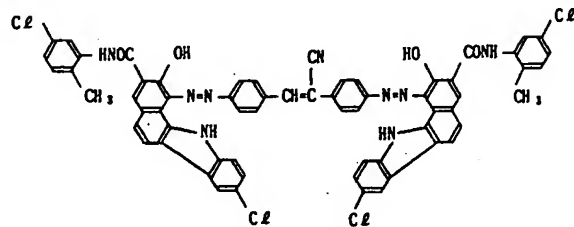
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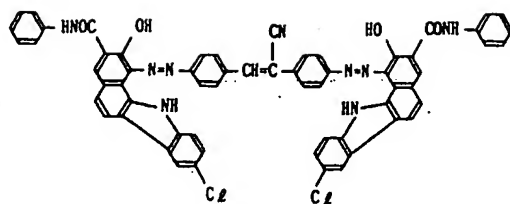
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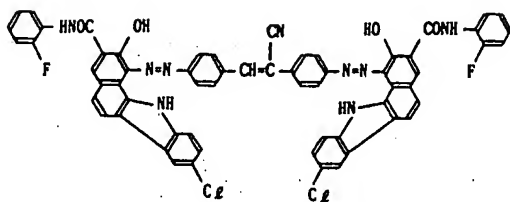
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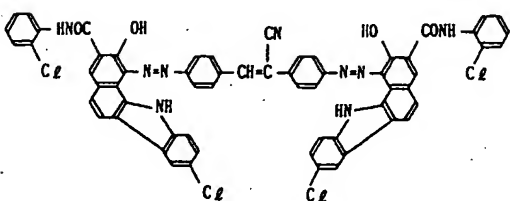
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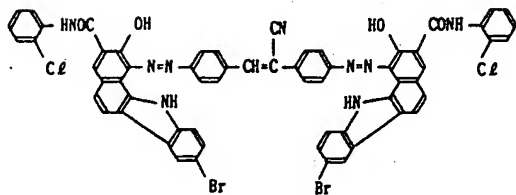
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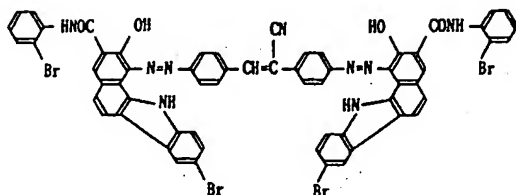
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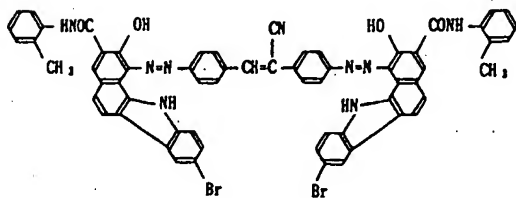
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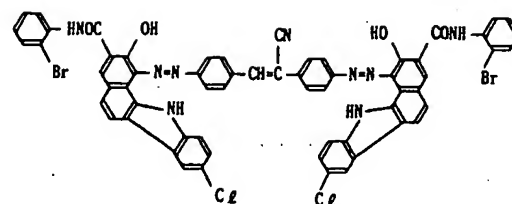
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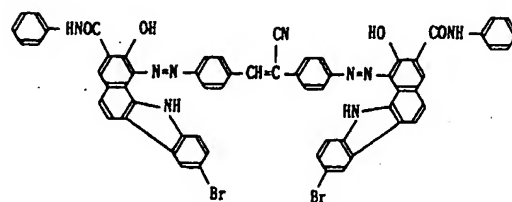
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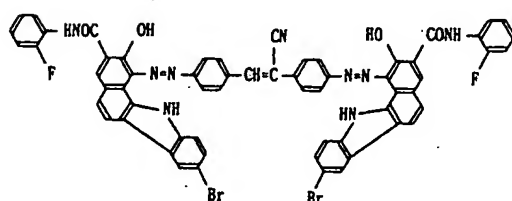
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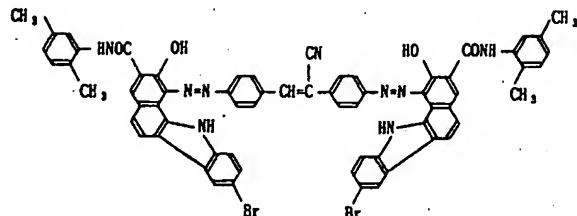
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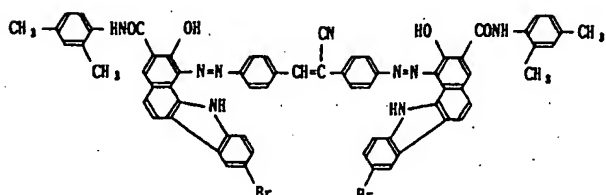
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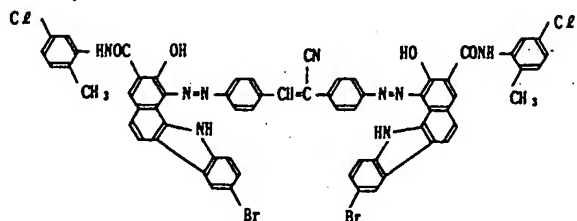
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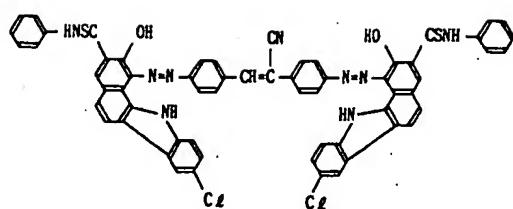
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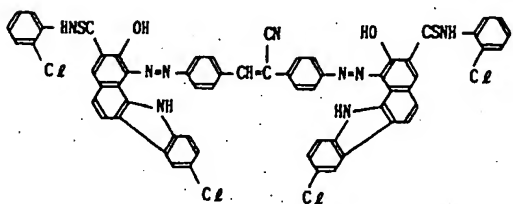
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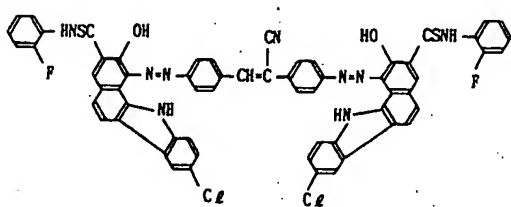
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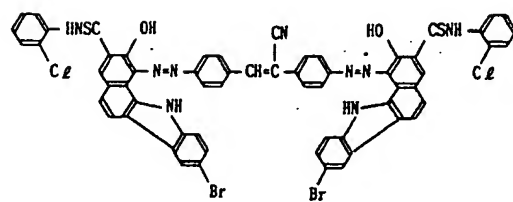
G-26



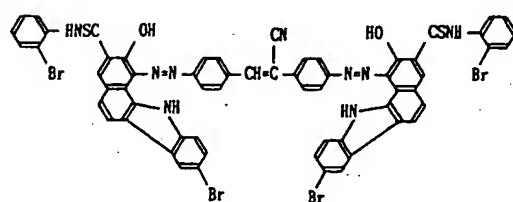
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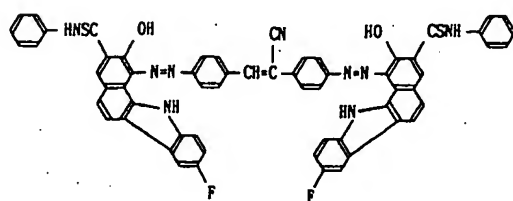
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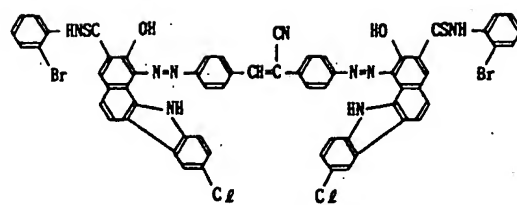
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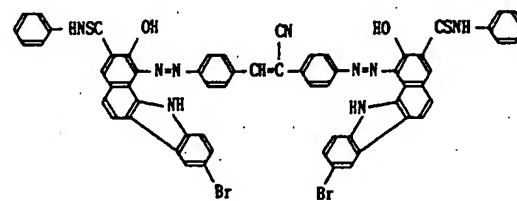
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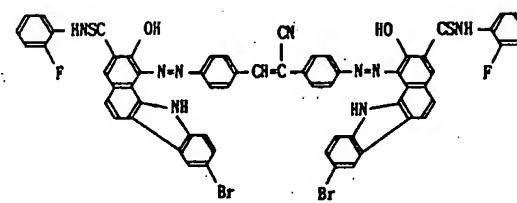
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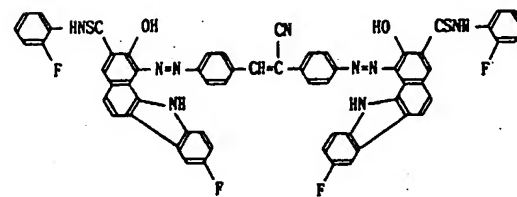
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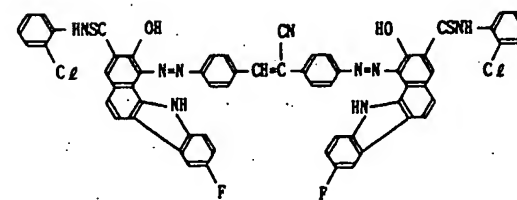
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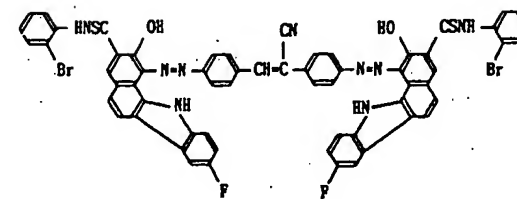
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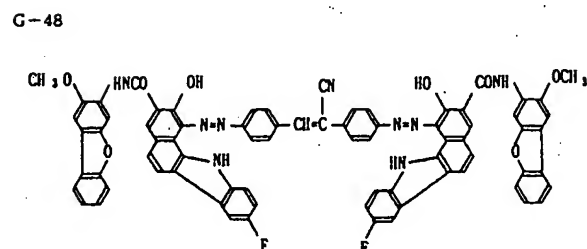
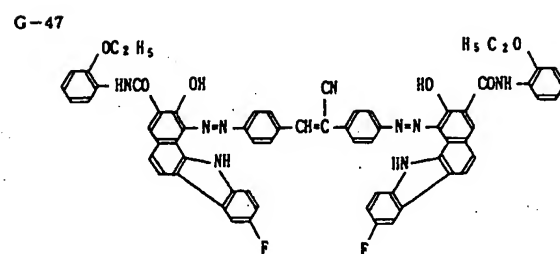
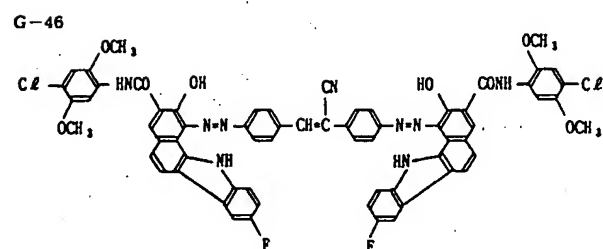
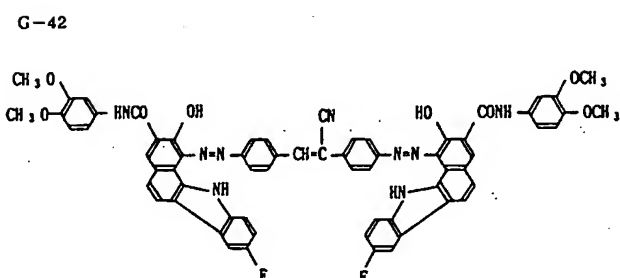
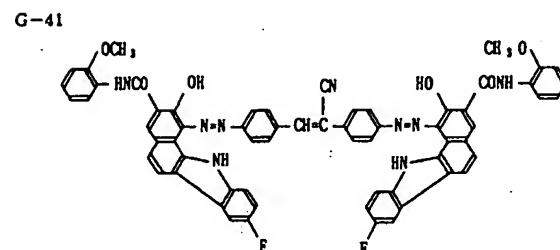
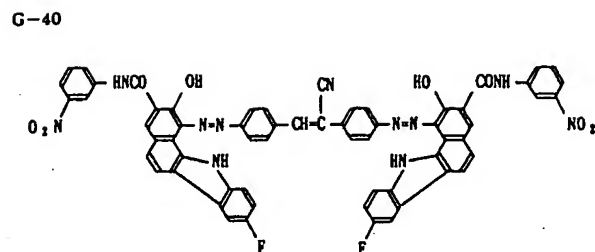
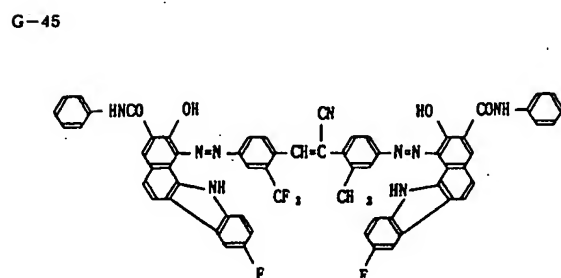
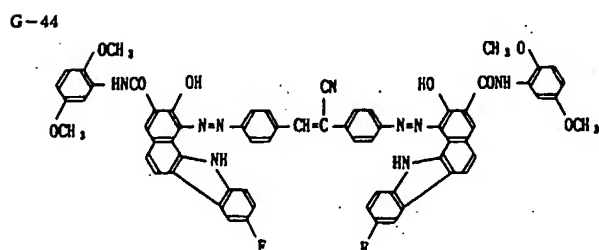
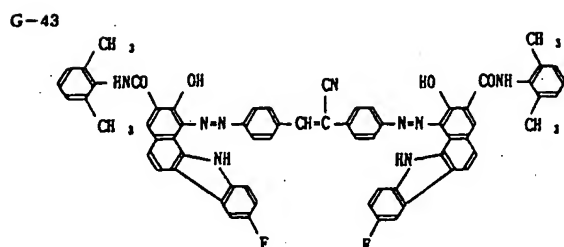
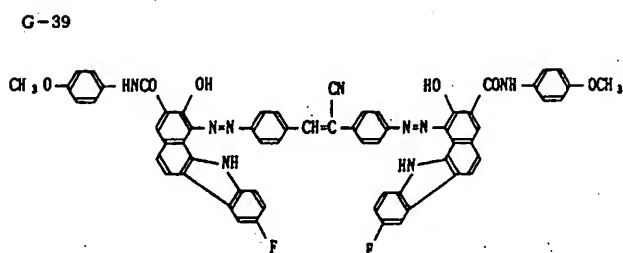
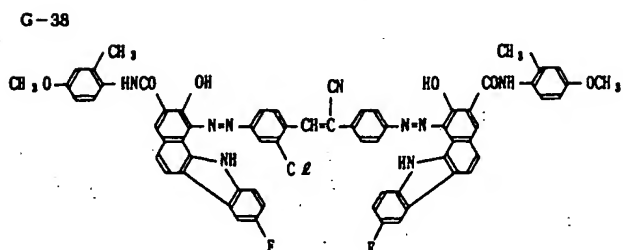
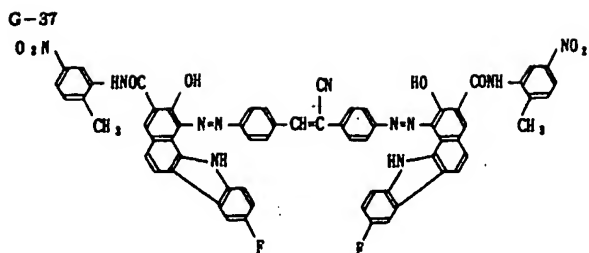


G-35



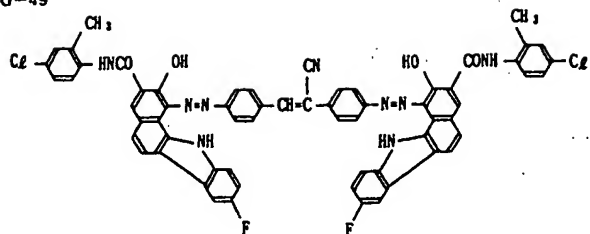
G-36



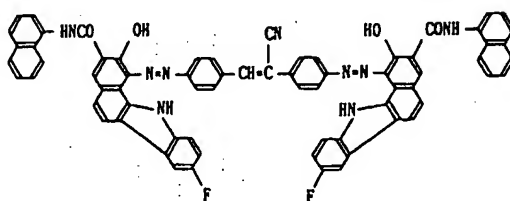




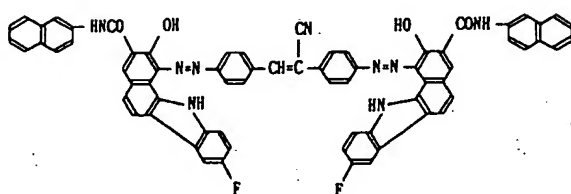
G-49



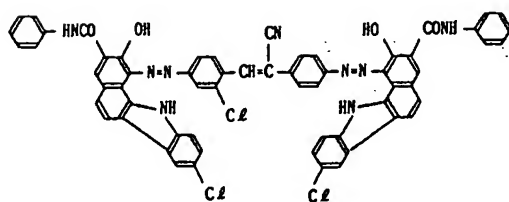
G-50



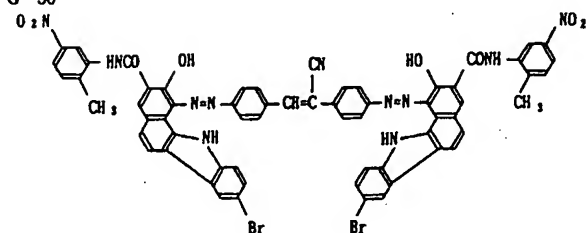
G-51



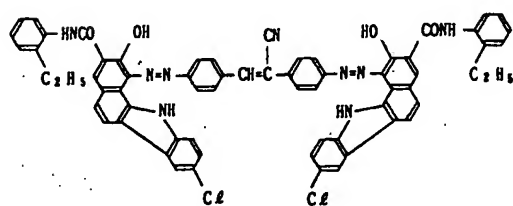
G-55



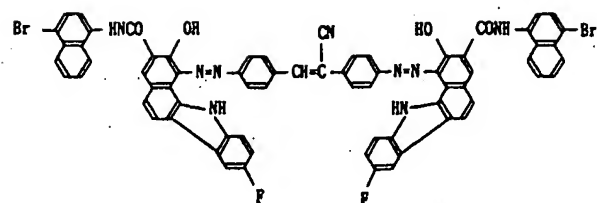
G-56



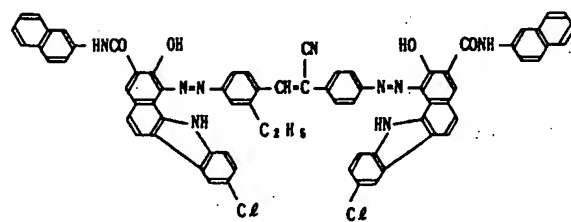
G-57



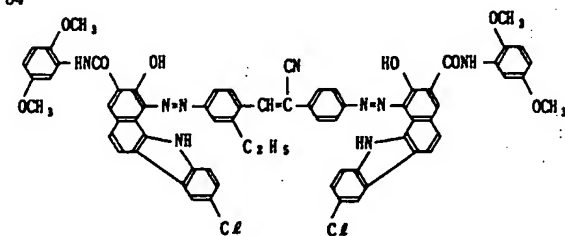
G-62



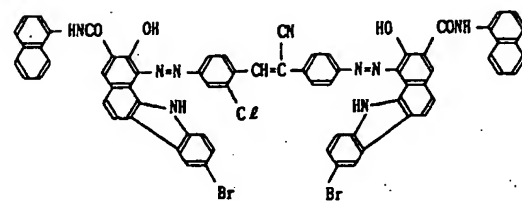
G-63



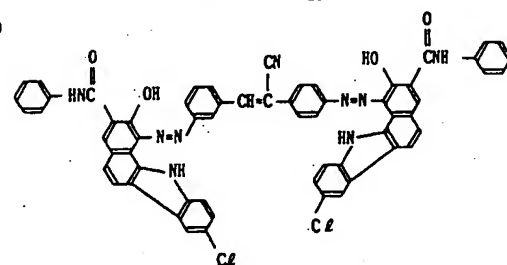
G-64



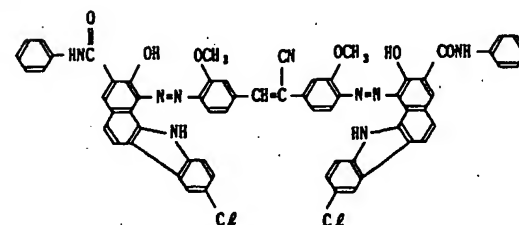
G-68



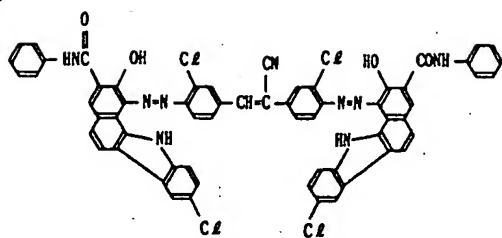
G-69



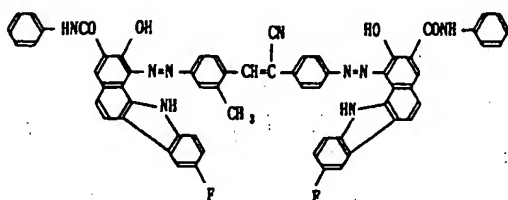
G-60



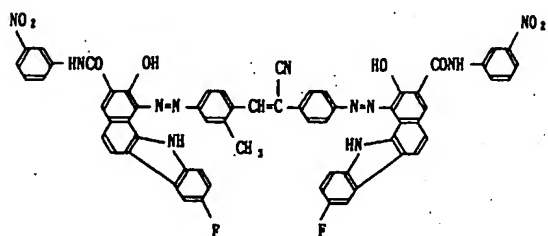
G-61



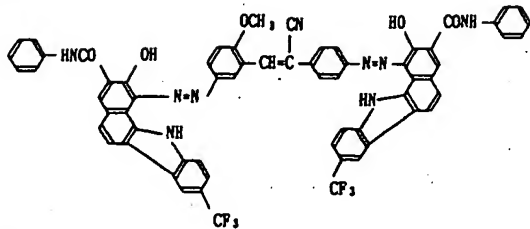
G-62



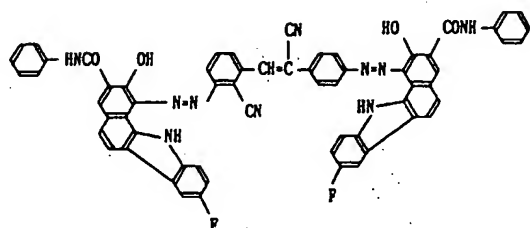
G-63



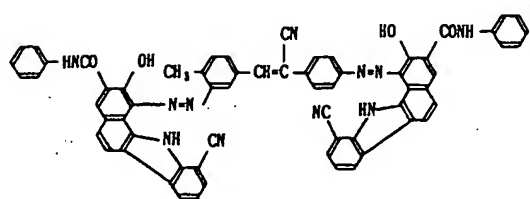
G-67



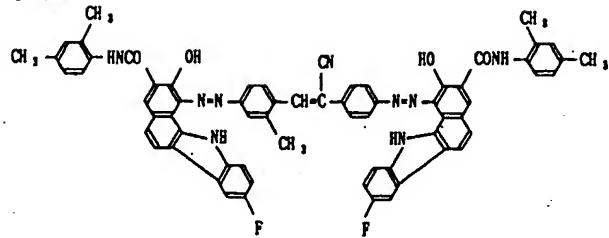
G-68



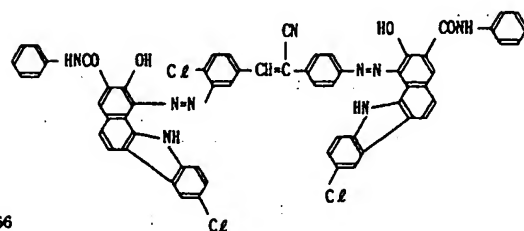
G-69



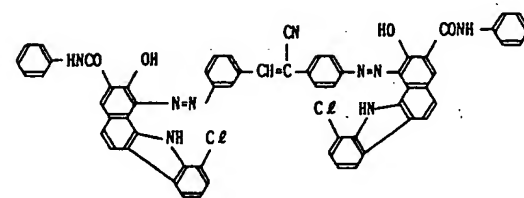
G-64



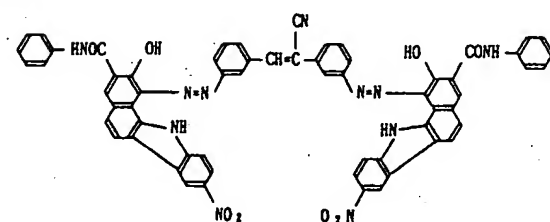
G-65



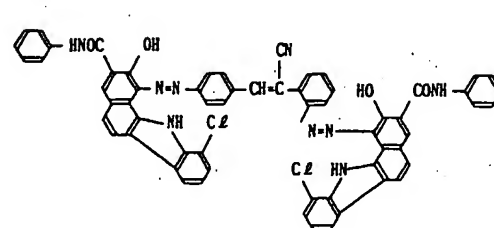
G-66



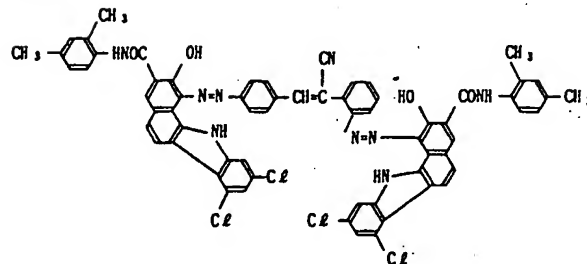
G-70



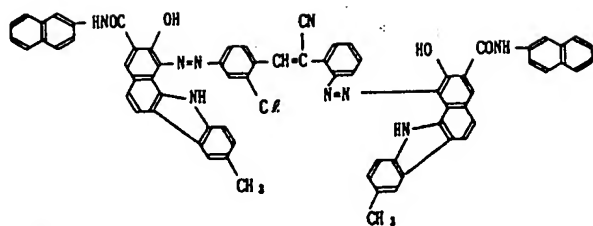
G-71



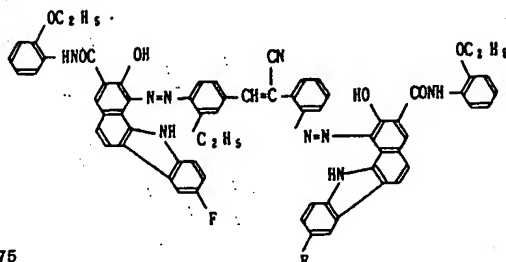
G-72



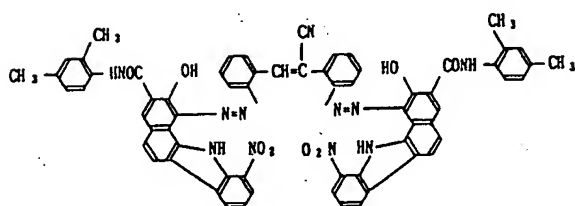
G-73



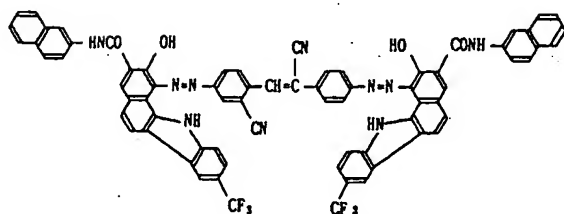
G-74



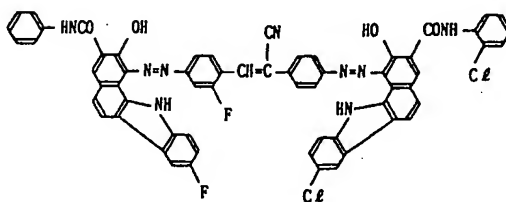
G-75



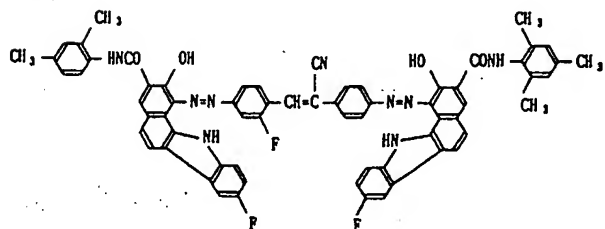
G-79



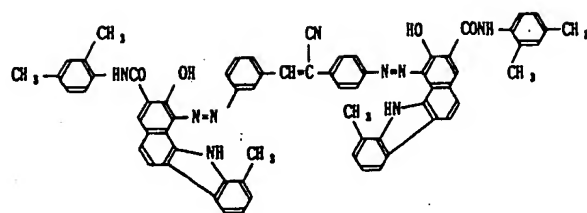
G-80



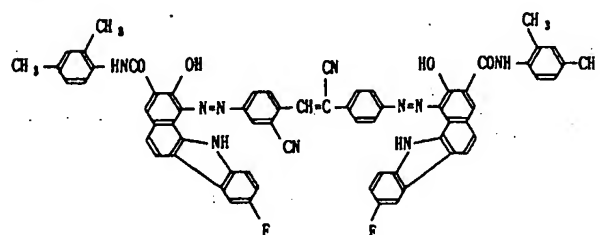
G-81



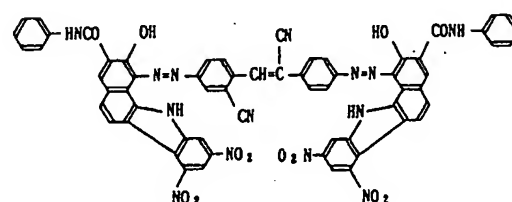
G-76



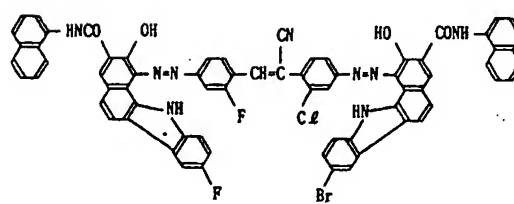
G-77



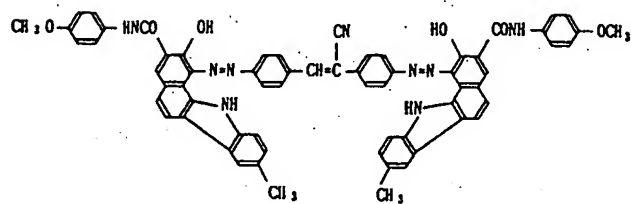
G-78



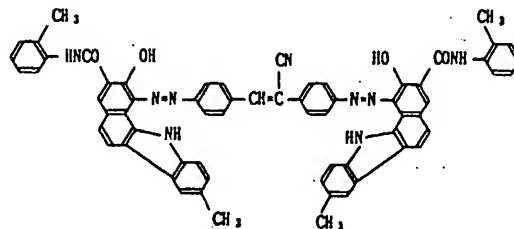
G-82

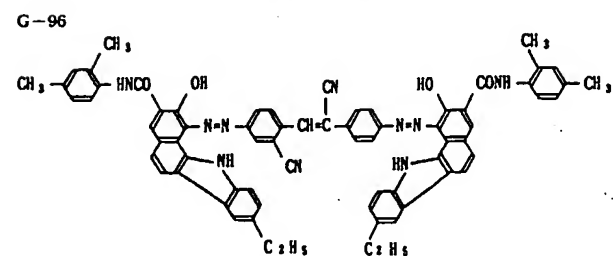
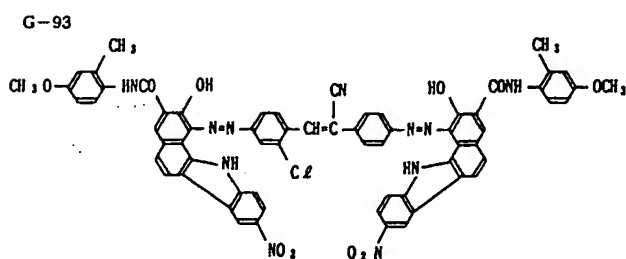
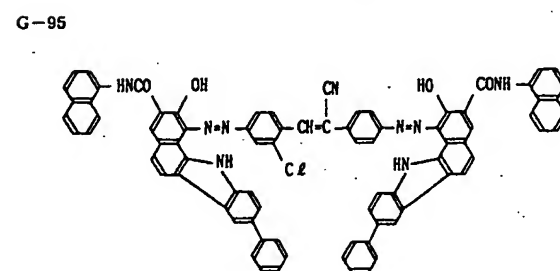
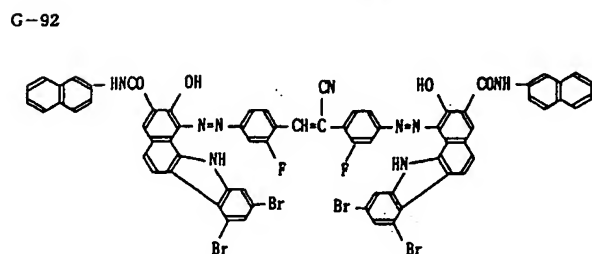
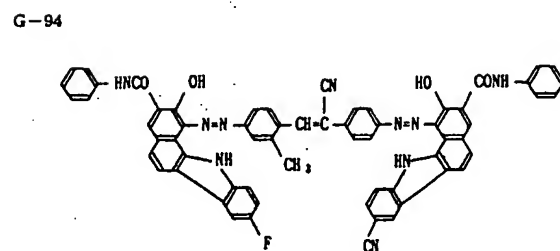
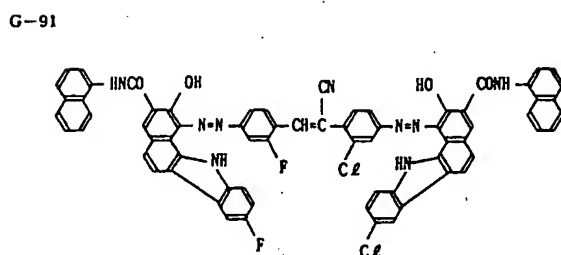
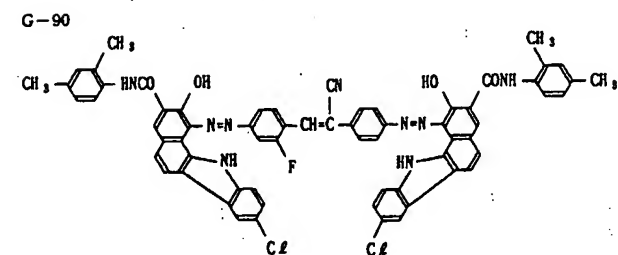
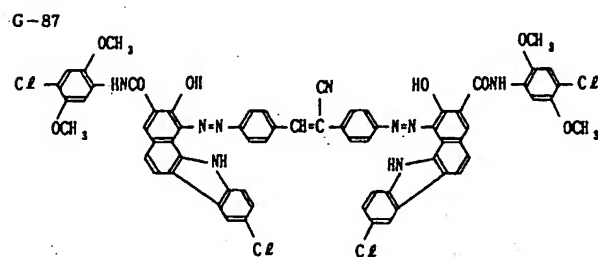
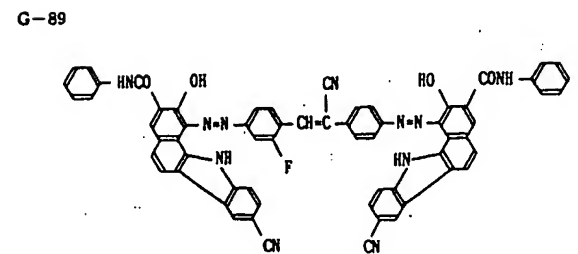
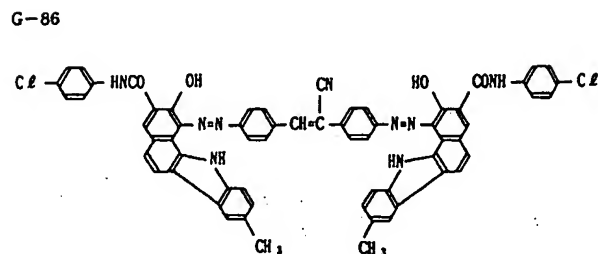
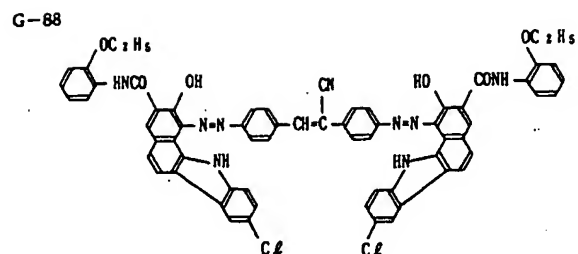
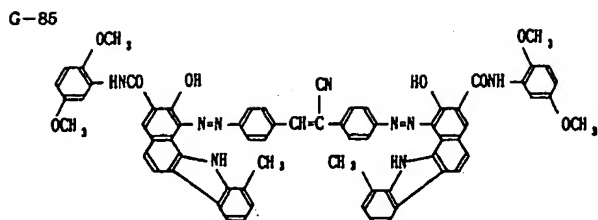


G-83

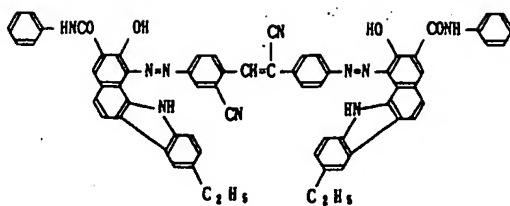


G-84

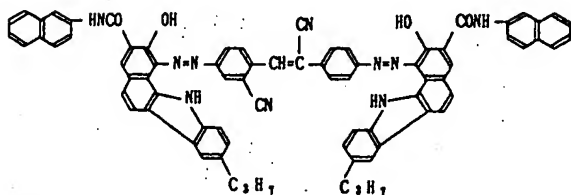




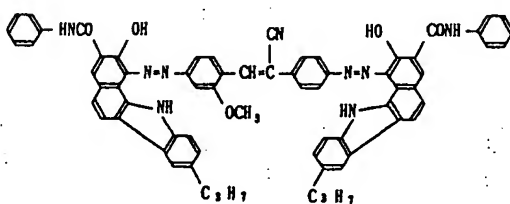
G-97



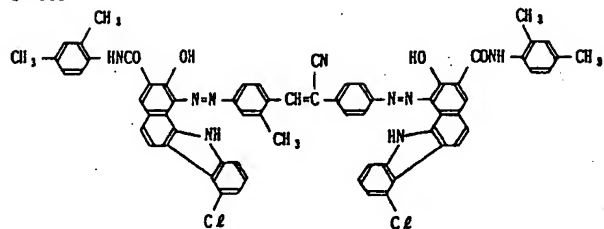
G-98



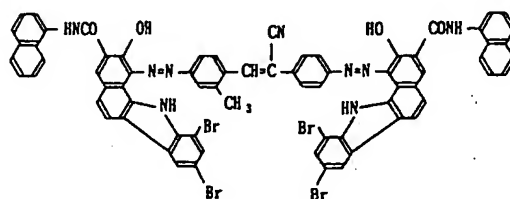
G-99



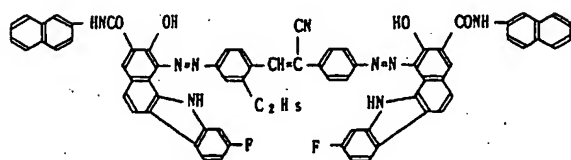
G-103



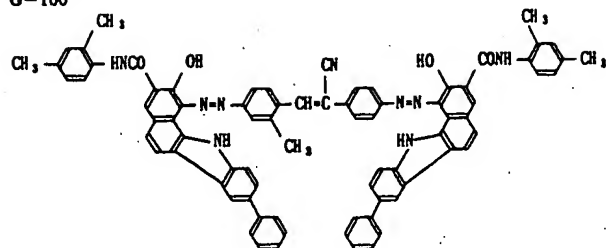
G-104



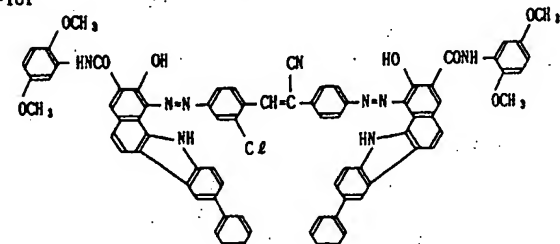
G-105



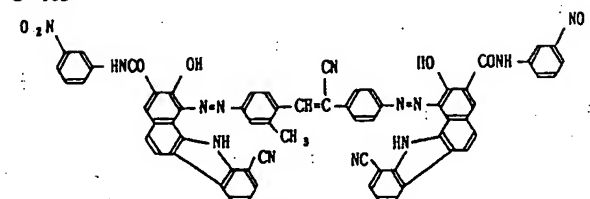
G-100



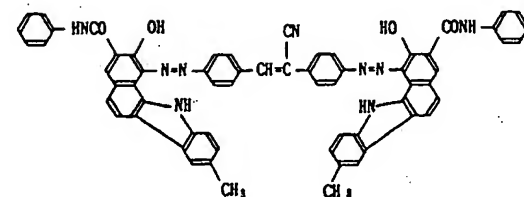
G-101



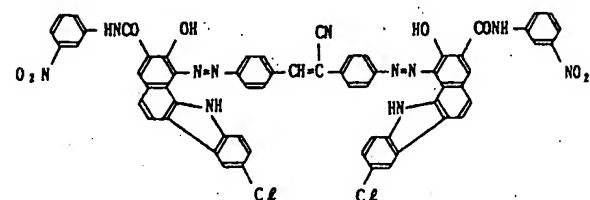
G-102



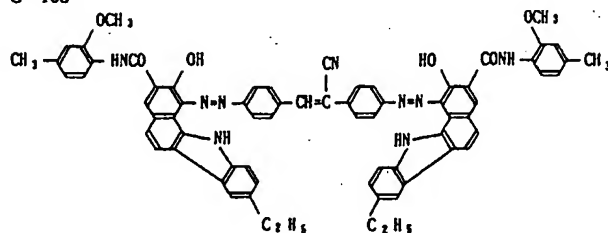
G-106



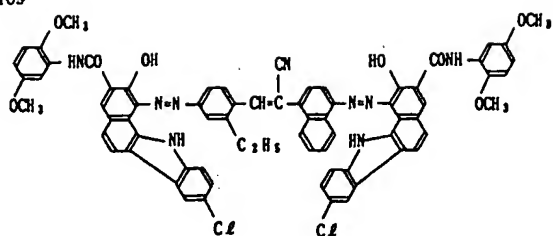
G-107



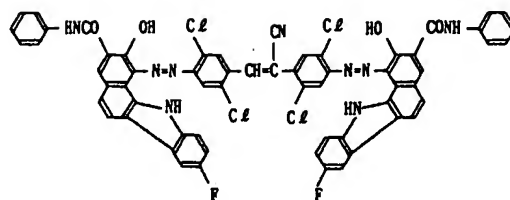
G-108



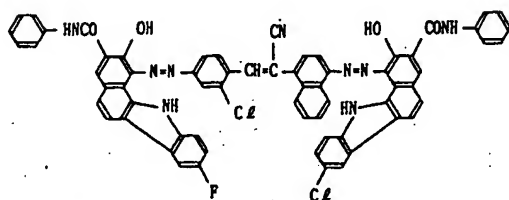
G-109



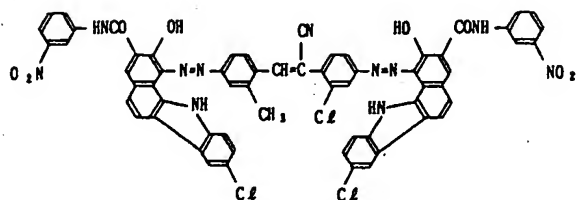
G-112



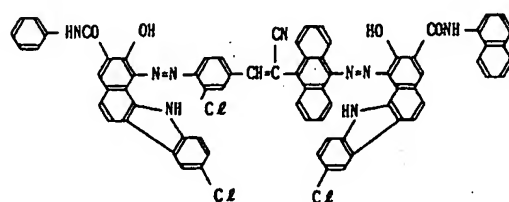
G-110



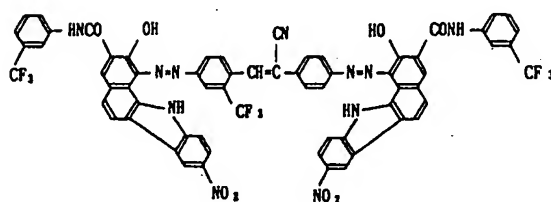
G-113



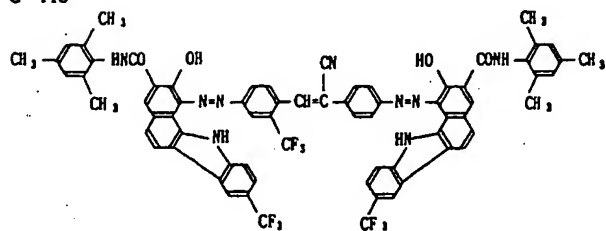
G-111



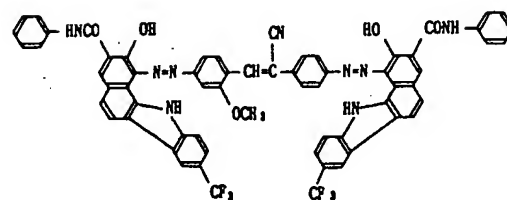
G-114



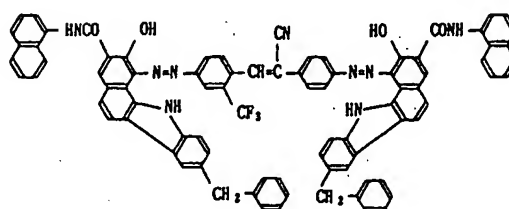
G-115



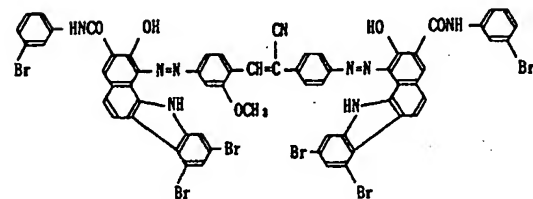
G-118



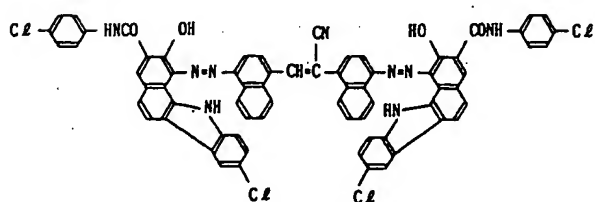
G-116



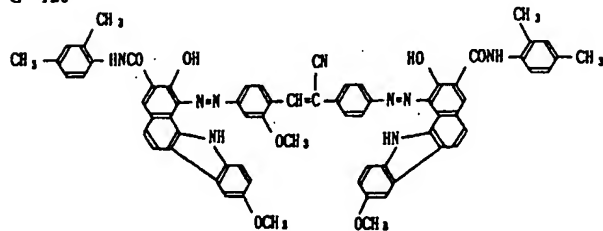
G-119



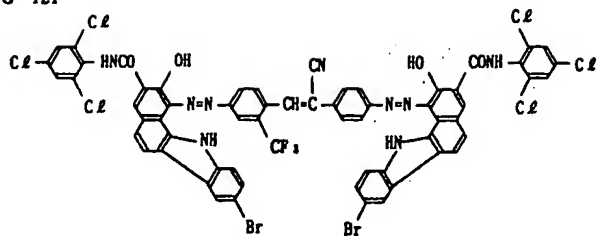
G-117



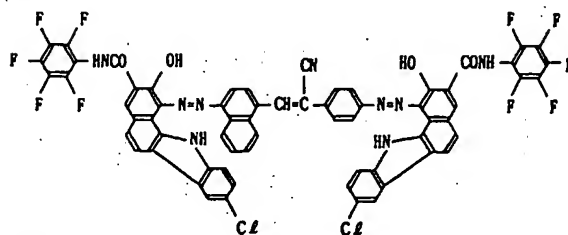
G-120



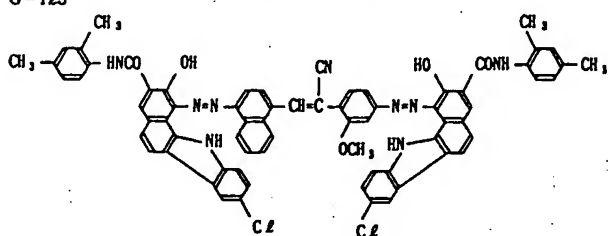
G-121



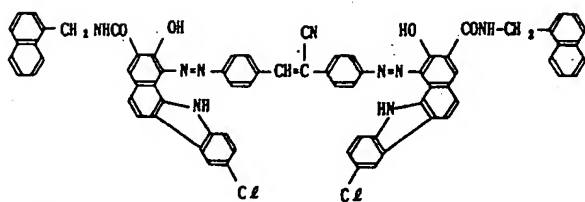
G-122



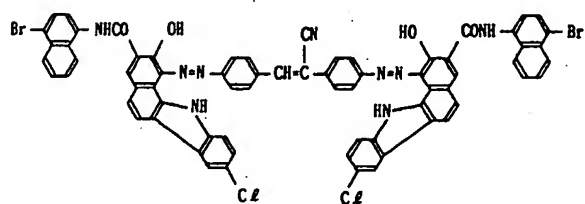
G-123



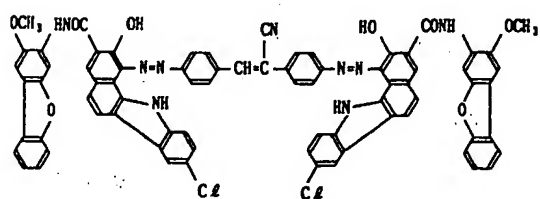
G-127



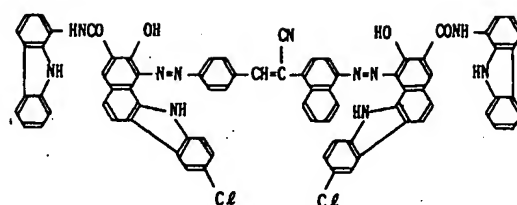
G-128



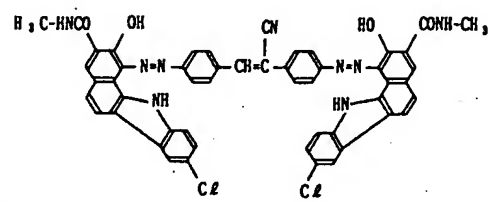
G-129



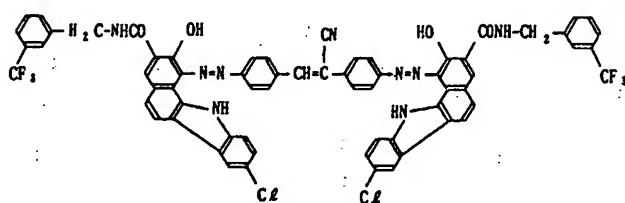
G-124



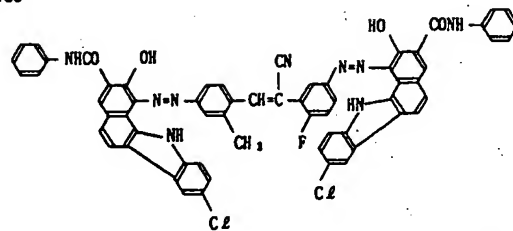
G-125



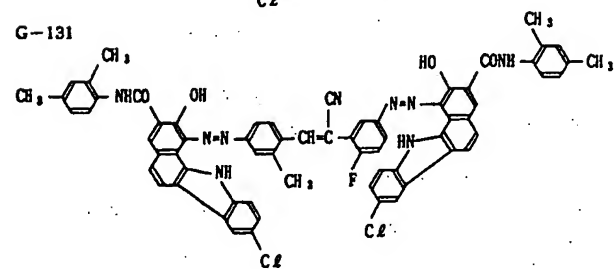
G-126



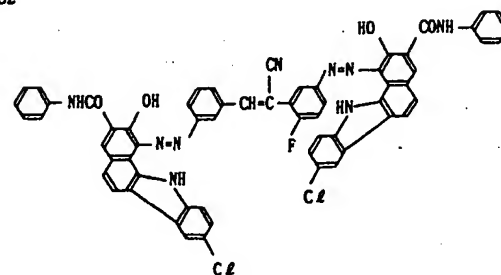
G-130



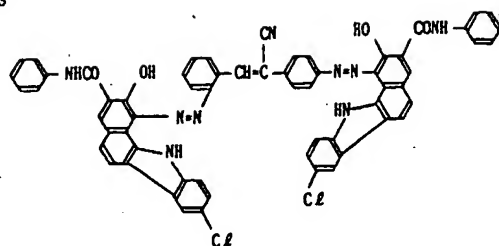
G-131



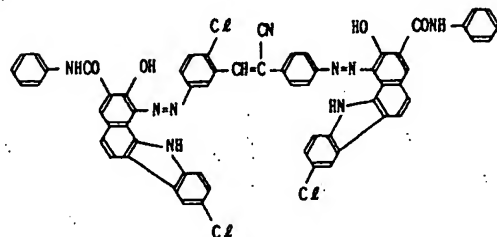
G-132



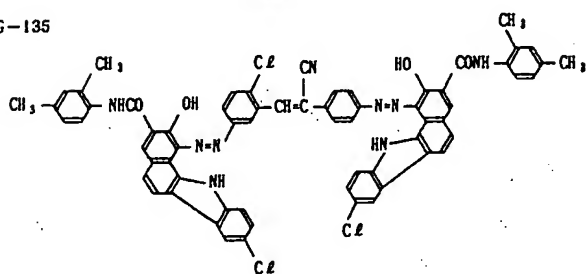
G-133



G-134

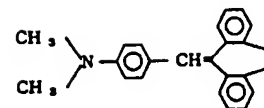


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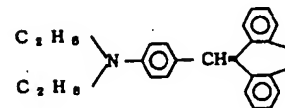


## 電荷輸送物質

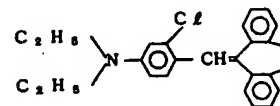
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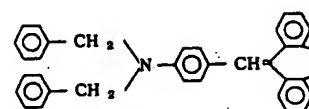
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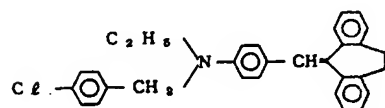
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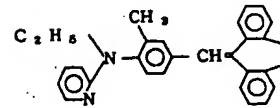
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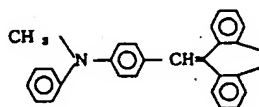
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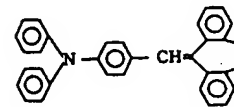
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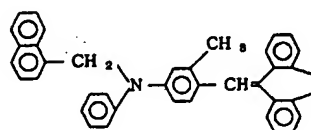
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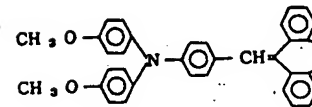
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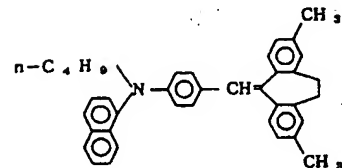
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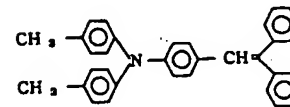
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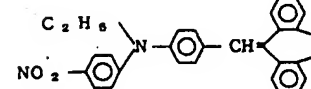
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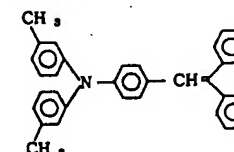
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T-9

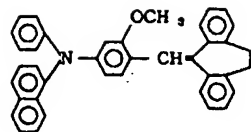


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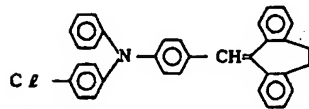




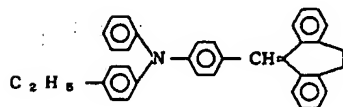
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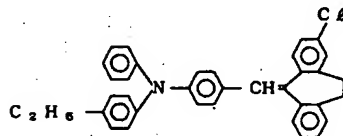
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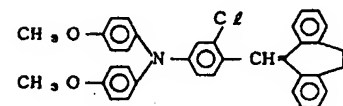
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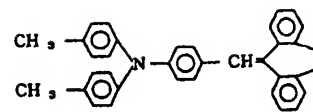
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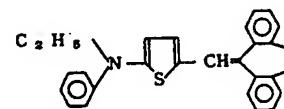
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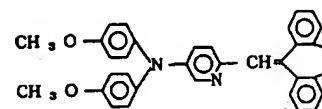
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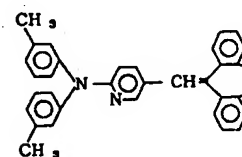
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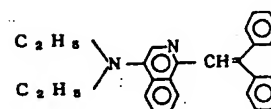
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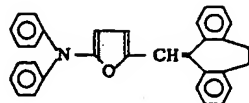
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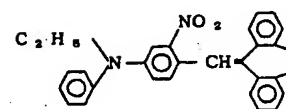
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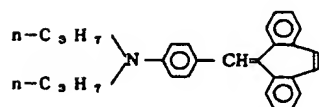
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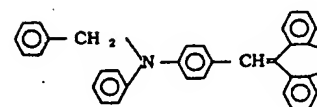
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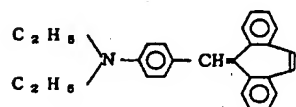
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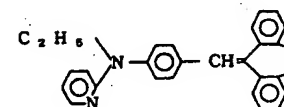
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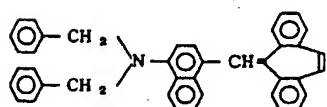
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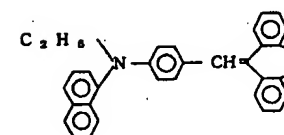
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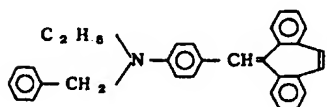
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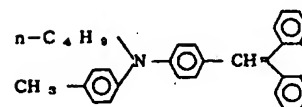
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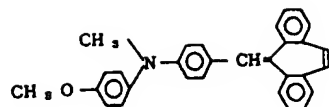
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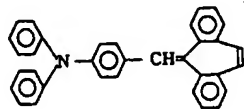
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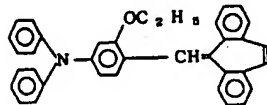
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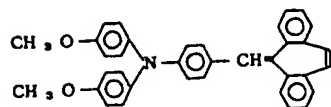
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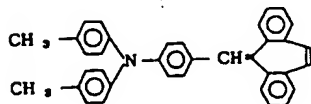
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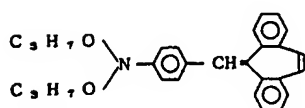
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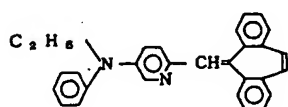
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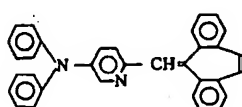
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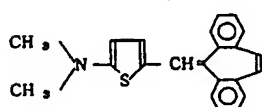
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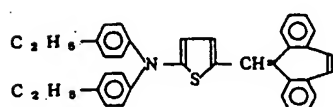
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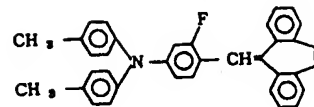
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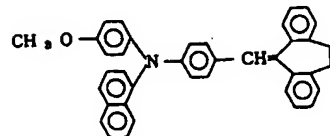
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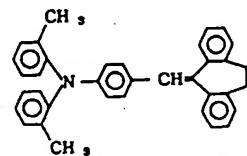
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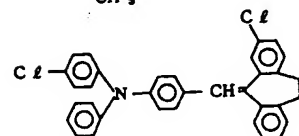
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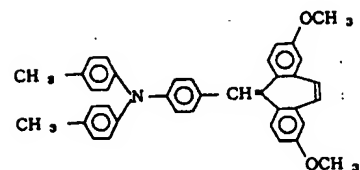
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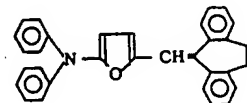
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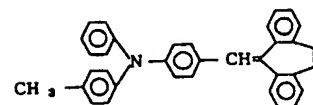
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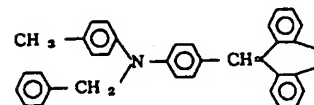
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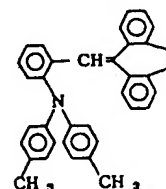
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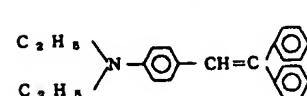
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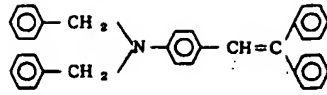
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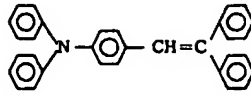
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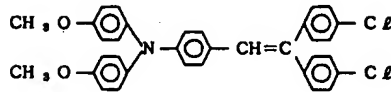
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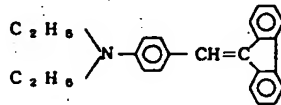
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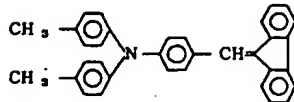
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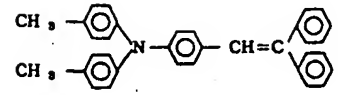
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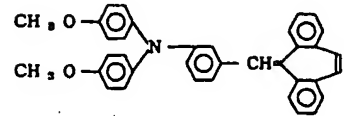
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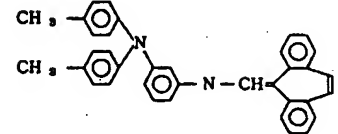
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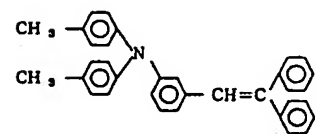
T-61



T-62



T-63



以下に本発明の電子写真感光体を図面を用いて説明する。

第1図は本発明の電子写真感光体の層構成を模式的に表わした図である。

一般式(1)で示されるジスアゾ顔料を含有する電荷発生層2は、十分な吸光度を得るために、できる限り多くの前述の光導電性を示す化合物を含有し、且つ発生した電荷キャリアの飛程を短くするために薄膜層、例えば $5\mu\text{m}$ 以下、好ましくは $0.01\mu\text{m}\sim 1\mu\text{m}$ の膜厚をもつ薄膜層とすることが好ましい。

電荷発生層2は、前述のジスアゾ顔料を適当なバインダーに分散させ、これを支持体の上に塗工することによって形成でき、また真空蒸着装置により蒸着膜を形成することによって得ることができる。電荷発生層を塗工によって形成する際に用いるバインダーとしては広範な絶縁性樹脂から選択でき、またポリ-N-ビニルカルバゾール、ポリビニルアントラセンやポリビニルピレンなどの有機光導電性ポリマーから選択できる。好ましく

は、ポリビニルブチラール、ポリアリレート(ビスフェノールAとフタル酸の縮重合体など)、ポリカーボネート、ポリエステル、フェノキシ樹脂、ポリ酢酸ビニル、アクリル樹脂、ポリアクリルアミド樹脂、ポリアミド、ポリビニルピリジン、セルロース系樹脂、ウレタン樹脂、エポキシ樹脂、カゼイン、ポリビニルアルコール、ポリビニルピロリドンなどの絶縁性樹脂を挙げることができる。電荷発生層中に含有する樹脂は、80重量%以下、好ましくは40重量%以下が適している。

これらの樹脂を溶解する溶剤は、樹脂の種類によって異なり、また下述の電荷輸送層や下引層を溶解しないものから選択することが好ましい。具体的な有機溶剤としては、メタノール、エタノール、イソプロパノールなどのアルコール類、アセトン、メチルエチルケトン、シクロヘキサノンなどのケトン類、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミドなどのアミド類、ジメチルスルホキシドなどのスルホキシド類、テトラヒドロフラン、ジオキサン、エチレングリコールモ

ノメチルエーテルなどのエーテル類、酢酸メチル、酢酸エチルなどのエステル類、クロロホルム、塩化メチレン、ジクロルエチレン、四塩化炭素、トリクロルエチレンなどの脂肪族ハロゲン化炭化水素類あるいはベンゼン、トルエン、キシレン、リグロイン、モノクロルベンゼン、ジクロルベンゼンなどの芳香族類などを用いることができる。

塗工は、浸漬コーティング法、スプレーコーティング法、マイヤーバーコーティング法、ブレードコーティング法などのコーティング法を用いて行うことができる。乾燥は室温における指触乾燥後、加熱乾燥する方法が好ましい。加熱乾燥は、30℃～200℃の温度で5分～2時間の範囲の時間で、静止または送風下で行うことができる。

電荷輸送層3は、前述の電荷発生層2と電気的に接続されており、電界の存在下で電荷発生層から注入された電荷キャリアを受け取るとともに、これらの電荷キャリアを表面まで輸送できる機能を有している。この際、この電荷輸送層3は、電荷発生層2の上に積層されているのが好ましいが、電

この様な電荷発生層2と電荷輸送層3の積層構造からなる感光層4は、導電性支持体1の上に設けられる。導電性支持体1としては、支持体自体が導電性をもつもの、例えばアルミニウム、アルミニウム合金、ステンレスなどを用いることができ、その他にアルミニウム、アルミニウム合金、酸化インジウム、酸化錫、酸化インジウム-酸化錫合金などを真空蒸着法によって被膜形成された層を有するプラスチック、導電性粒子（例えば、カーボンブラック、銀粒子など）を適当なバインダーとともにプラスチックや前記金属支持体の上に被覆した支持体、導電性粒子をプラスチックや紙に含浸した支持体や導電性ポリマーを有するプラスチックなどを用いることができる。

導電性支持体1と感光層4の中間に、バリアー機能と接着機能をもつ下引層を設けることもできる。下引層は、カゼイン、ポリビニルアルコール、ニトロセルロース、エチレン-アクリル酸コポリマー、ポリアミド（ナイロン6、ナイロン66、ナイロン610、共重合ナイロン、アルコキシメチル化ナイ

ロルなど）、ポリウレタン、ゼラチン、酸化アルミニウムなどによって形成できる。

電荷輸送層3は前述の電荷輸送物質を適当なバインダーと共に溶解塗布し形成することができる。

バインダーとして使用できる樹脂は、例えばアクリル樹脂、ポリアリレート、ポリエステル、ポリカーボネート、ポリスチレン、アクリロニトリル-スチレンコポリマー、アクリロニトリル-タジエンコポリマー、ポリビニルブチラール、ポリビニルホルマール、ポリスルホン、ポリアクリルアミド、ポリアミド、塩素化ゴムなどの絶縁性樹脂、あるいはポリ-N-ビニルカルバゾール、ポリビニルアントラセン、ポリビニルピレンなどの有機光導電性ポリマーを挙げることができる。

電荷輸送層3は、電荷キャリアを輸送できる限界があるので、必要以上に膜厚を厚くすることができない。一般的には、5 $\mu$ m～35 $\mu$ mであるが、好ましい範囲は8 $\mu$ m～30 $\mu$ mである。塗工によって電荷輸送層を形成する際には、前述した様な適当なコーティング法を用いることができる。

（実施例）

以下本発明を実施例によって説明する。

本発明の電子写真感光体は電子写真複写機に利用するのみならずレーザープリンターやLEDプリンター、液晶プリンター、レーザー製版等の電子写真応用分野にも広く利用できるが特にLEDプリンターに用いることで性能を十分に発現させることができる。

（実施例）

以下本発明を実施例によって説明する。

実施例1

アルミ板上に0.1 $\mu$ mの塩化ビニル-無水マレイン酸-酢酸ビニル共重合体樹脂よりなる下引層を設けた。

次に前記例示のジスアゾ顔料（G-13）5gをシクロヘキサノン95mlにブチラール樹脂（ブチラール化度63モル%、数平均分子量20000）2gを溶かした液に加えサンドミルで20時間分散した。

この分散液を先に形成した下引層の上に乾燥後の膜厚が $0.5\mu\text{m}$ となるようにマイヤーバーで塗布し乾燥して電荷発生層を形成した。

次いで、前記例示のスチリル化合物 (T-39) 5gとビスフェノールZ型ポリカーボネート樹脂 (粘度平均分子量30000) 5gをクロロベンゼン70mlに溶解し、これを電荷発生層の上に乾燥後の膜厚が $22\mu\text{m}$ となるようにマイヤーバー塗布し乾燥して電荷輸送層を形成し感光体No.1を作製した。

この様にして作製した電子写真感光体を川口電機製静電複写紙試験装置 Model SP-428を用いてスタティック方式で $-5.6\text{KV}$ のコロナ帯電し、暗所で1時間保持した後、照度 $2\text{lux}$ のハロゲンランプで露光し帯電特性を調べた。帯電特性としては表面電位 ( $V_0$ ) と1秒間暗減衰させた時の電位 ( $V_D$ ) を $\frac{1}{2}$ に減衰するに必要な露光量 ( $E_{\frac{1}{2}}$ ) を測定した。

結果を以下に示す。

いずれの環境においてもオリジナルに忠実な良好な画像が得られた。この画像は1万枚目においても画像のにじみ、ボケ等はみられず本感光体が良好な画像特性を示すことがわかった。

#### 実施例2

実施例1のジスアゾ顔料 (G-13) にかえて、ジスアゾ顔料 G-10, G-11, G-19 および G-14 をそれぞれ用いる以外は実施例1と全く同様にして感光体を作製し帯電特性と分光感度を測定した。帯電特性を第1表に、分光感度を第3図に示す。

第1表

実施例	感光体No.	ジスアゾ顔料	$V_0(\text{V})$	$V_D(\text{V})$	$E_{\frac{1}{2}}(\text{lux} \cdot \text{sec})$
2	2	G-10	-720	-690	1.34
3	3	G-11	-740	-704	2.11
4	4	G-14	-700	-650	1.55
5	5	G-19	-700	-680	0.90

#### 比較例1および2

特開昭59-157644号公報記載の下記比較ジスアゾ顔料 (1)

$$V_0: -720\text{V}$$

$$V_D: -700\text{V}$$

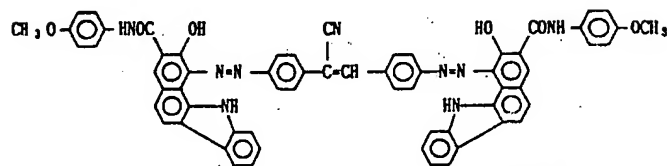
$$E_{\frac{1}{2}}: 0.99\text{lux} \cdot \text{sec}$$

次に、先の静電複写紙試験装置の光源に光強度 $1\mu\text{W}/\text{cm}^2$ の単色光を用い分光感度を測定した。感度は表面電位 ( $V_D$ ) を $-700\text{V}$ とし表面電位が $-200\text{V}$ になるのに要する露光量  $E_{\Delta 500\text{V}}(\mu\text{J}/\text{cm}^2)$  を測定し、

$$E(\text{V} \cdot \text{cm}^2/\mu\text{J}) = \frac{500(\text{V})}{E_{\Delta 500\text{V}}(\mu\text{J}/\text{cm}^2)}$$

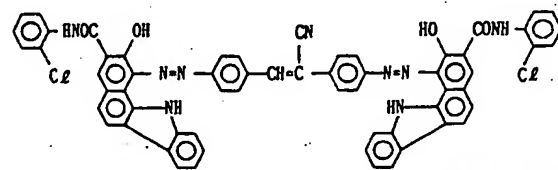
を計算し、波長に対しプロットした結果を第2図に示す。

さらに本感光体を $-5.6\text{KV}$ のコロナ帯電器、露光光学系、現像機、転写帯電器、除電露光光学系およびクリーナーを備えた電子写真複写機のシリンドラに貼り付け画像特性を調べた。この複写機はシリンドラの駆動に伴い転写紙上に画像が得られる構成になっている。この複写機を用いた画像特性の評価は湿度10% 気温5℃、湿度50% 気温18℃、湿度80% 気温35℃の三環境にて行った。



比較顔料 (1)

を用いる以外は実施例1と全く同様にして感光体を作製し比較試料1とし実施例1と同様にして帯電特性を調べた。さらに下記構造の比較顔料 (2) についても同様の評価を行った。



比較顔料 (2)

結果を第2表に示す。

第 2 表

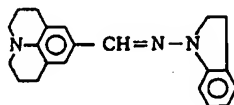
比較例	比較感光体№	比較顔料№	V <sub>0</sub> (V)	V <sub>D</sub> (V)	E% (lux・sec)
1	1	1	-730	-720	7.06
2	2	2	-720	-700	3.90

第1表および第2表より、本発明による電子写真感光体は大きな感度を有するものであることがわかる。

実施例6～10

実施例1～5および比較例1, 2で用いた感光体をコロナ帯電器、露光光学系、現像器、転写帯電器、除電露光光学系およびクリーナーを備えた電子写真機のシリンダーに感光体を貼りつけた。この複写機はシリンダーの駆動に伴い、転写紙上に画像が得られる構成になっている。この複写機を用いて初期の明部電位(V<sub>L</sub>)と暗部電位(V<sub>D</sub>)をそれぞれ-200V, -700Vに設定し1万回使用した後の明部電位(V<sub>L</sub><sup>10000</sup>)と暗部電位(V<sub>D</sub><sup>10000</sup>)の変動量ΔV<sub>L</sub>、ΔV<sub>D</sub>を測定した。この結果を第3表に示す。尚ΔV<sub>D</sub>、ΔV<sub>L</sub>における負記号

6～10と全く同様にして電位変動量を測定した。結果を第4表に示す。



第 4 表

比較例	比較感光体№	アゾ顔料№	V <sub>0</sub> (V)	V <sub>D</sub> (V)	E% (lux・sec)	ΔV <sub>D</sub> (V)	ΔV <sub>L</sub> (V)
5	3	G-13	-700	-630	1.70	-20	+15
6	4	G-10	-700	-640	2.73	-20	+5
7	5	G-11	-690	-660	3.99	-30	+20
8	6	G-14	-730	-660	3.20	-5	+15
9	7	G-19	-700	-640	1.51	-10	+20
10	1	比較顔料1	-700	-560	10.5	-90	+80
11	2	比較顔料2	-690	-500	6.25	-60	+100

第4表より本発明のジスアゾ顔料とステリル化合物とを組合わせることで優れた特性を有する感光体を得ることができる。さらに本発明のジスアゾ顔料では、電荷輸送物質が変わっても特性の劣化

は電位の低下を表わし、正記号は電位の上昇を表わす。

第 3 表

例	感光体№	ΔV <sub>D</sub> (V)	ΔV <sub>L</sub> (V)
実施例6	1	-6	+5
実施例7	2	-5	0
実施例8	3	-10	+7
実施例9	4	+5	0
実施例10	5	0	+5
比較例3	比較感光体1	-50	+60
比較例4	比較感光体2	-30	+50

第3表より、本発明のジスアゾ顔料を用いた感光体は繰返し使用時の電位変動が少ないことがわかる。

比較例5～11

実施例1～5、比較例1, 2で用いたステリル化合物(T-39)にかえて下記構造のヒトラゾン化合物を用いる以外は実施例1～5と全く同様にして感光体を作製し帯電特性を測定した。また実施例

が小さく電荷輸送物質の選択の幅が広いことがわかる。

実施例11

前記例示のジスアゾ顔料(G-45)5gをシクロヘキサノン100mlに混合しボールミルで10分間分散した。この分散液を乾燥後の膜厚が0.5μmになるようにアルミ板上に塗布しキャリア発生層を形成した。次いで前記例示電荷輸送物質T-6010gとビスフェノールA型ポリカーボネート樹脂(粘度平均分子量28000)10gを1,2-ジクロロエタン70mlに溶解し、この溶液を前記キャリア発生層の上に乾燥後の膜厚が18μmとなるように塗布してキャリア輸送層を形成させ本発明の電子写真感光体を作製した。

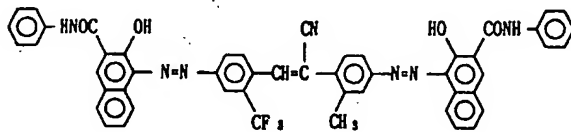
以上のようにして得られた感光体を実施例1と同様にして電子写真特性を測定した。さらに同様の測定を1000回繰り返して行った。さらに本実施例で用いた分散液を1カ月放置したのち、上記と同様の方法で感光体を作製し電子写真特性を測定した。結果は第5表に示すとおりである。

第 6 表

	第1回目	第1000回目	分散液を1ヵ月放置後	
			第1回目	第1000回目
V <sub>0</sub> (V)	-700	-695	-700	-696
V <sub>D</sub> (V)	-680	-678	-681	-677
E <sub>1/2</sub> (lux・sec)	1.9	1.9	1.9	1.9

## 比較例 12

キャリア発生物質として特開昭59-7365号公報記載の下記ビスアゾ顔料を用い実施例11と同様にして比較感光体を作製した。



この比較感光体について実施例11と同様にして測定を行ったところ第6表に示す結果を得た。

本発明のジスアゾ顔料はその分散状態での安定性が良く実用上すぐれた特性を示す。さらに本発明の感光体はアゾ顔料の置換基を選択することでLEDの発光波長域で高感度な電子写真感度を示す。

## 4. 図面の簡単な説明

第1図は電子写真感光体の層構成を示す模式図、第2図および第3図は実施例の分光感度を示す図である。

出願人 キヤノン株式会社

代理人 丸 島 勉 一



第 6 表

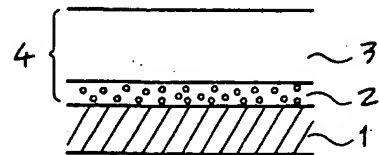
	第1回目	第1000回目	分散液を1ヵ月放置後	
			第1回目	第1000回目
V <sub>0</sub> (V)	-690	-600	-600	-540
V <sub>D</sub> (V)	-650	-580	-590	-500
E <sub>1/2</sub> (lux・sec)	2.5	2.6	4.0	4.1

以上の結果から明らかなように比較例のキャリア発生物質は分散時間が短かくても特性を出すことはできるが分散液の経時変化が大きく実用上大きな障害となる。本発明の電子写真感光体は分散時間が短かくても十分な特性を出すことができ、しかも分散液の経時変化がほとんど無く実用上優れたものである。

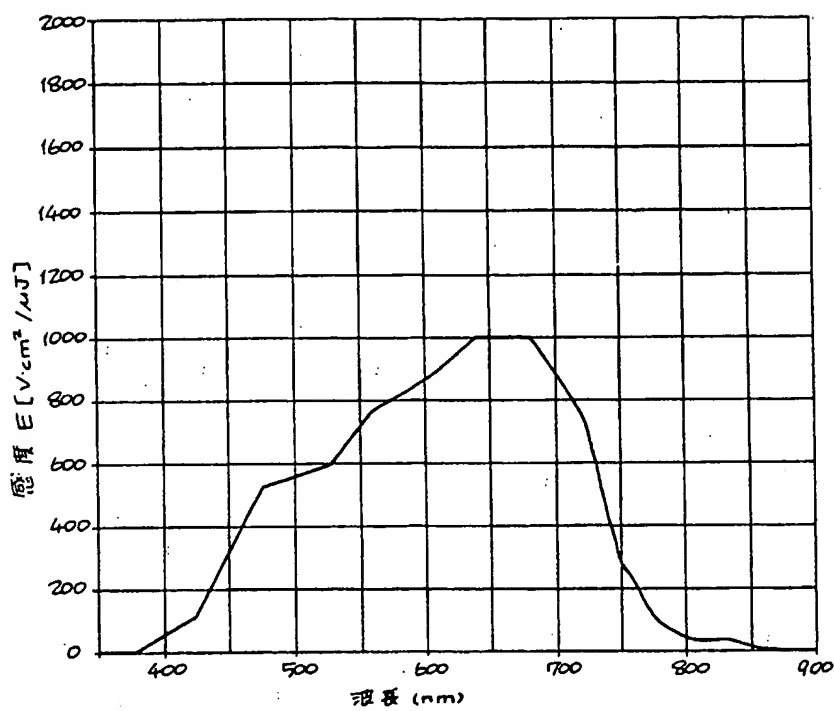
## 〔発明の効果〕

本発明によるジスアゾ顔料とスチリル化合物の組合せによれば感光層内部に於けるキャリア発生效率の向上、キャリア輸送効率の向上がはかられ、結果的に高感度で耐久性とりわけ電位安定性のすぐれた電子写真感光体を得ることができる。また

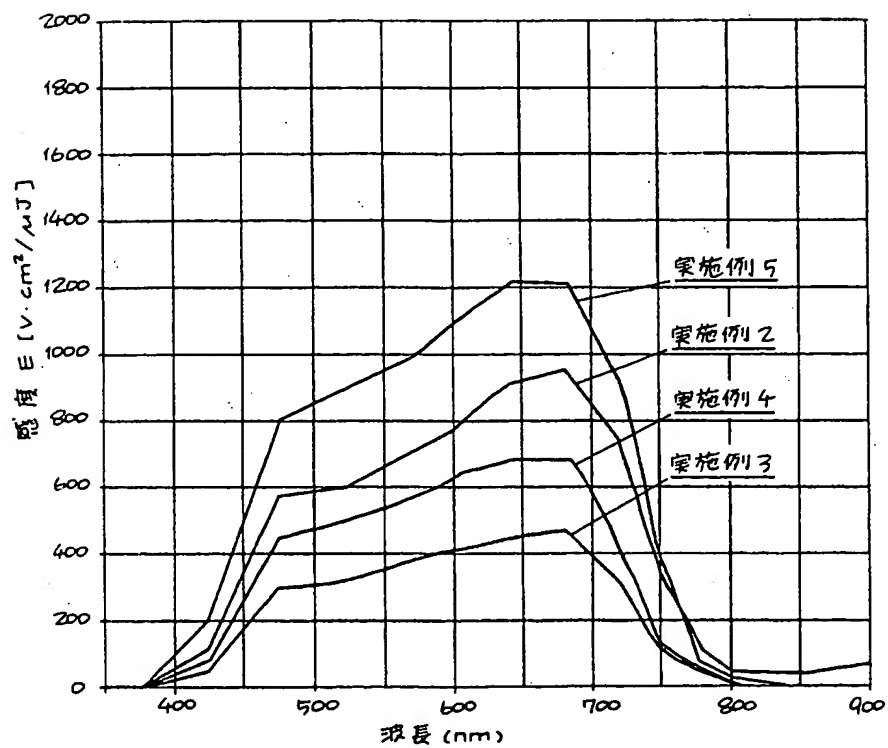
第1図



第2図



第3図





Japanese Kokai Patent Application No. Hei 2[1990]-113258A

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Job No.: 166-101332

Ref.: JP02113258A

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JAPANESE PATENT OFFICE  
PATENT JOURNAL (A)  
KOKAI PATENT APPLICATION NO. HEI 2[1990]-113258

Int. Cl <sup>5</sup> :	G 03 G 5/06
Sequence Nos. for Office Use:	6906-2H
Filing No.:	Sho 63[1988]-266720
Filing Date:	October 21, 1988
Publication Date:	April 25, 1990
No. of Claims:	2 (Total of 24 pages)
Examination Request:	Not filed

ELECTROPHOTOGRAPHIC PHOTSENSITIVE MATERIAL

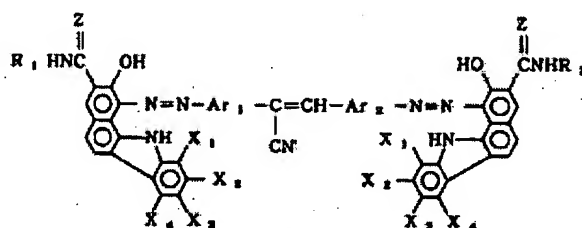
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Applicant:	Canon Inc. 3-30-2 Shimomaruko, Ota-ku, Tokyo
Agent:	Yoshiichi Marushima, patent attorney

[There are no amendments in this patent]

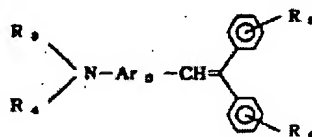
Claim

1. An electrophotographic photosensitive material, characterized in that in a lamination type electrophotographic photosensitive material having a charge generation layer and a charge

transport layer on a substrate, the charge generation layer contains, as a charge-generating material, a disazo pigment expressed by general formula (1)

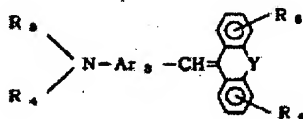


(wherein  $R_1$  and  $R_2$  represent alkyl groups, aralkyl groups, aromatic rings, or heterocyclic rings;  $Ar_1$  and  $Ar_2$  represent aromatic rings or heterocyclic rings;  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  represent hydrogen atoms, alkyl groups, alkoxy groups, halogen atoms, nitro groups, cyano groups or trifluoromethyl groups, as long as they do not all represent hydrogen atoms;  $Z$  represents an oxygen or sulfur atom), and the charge transport layer contains, as the charge-transporting material, a styryl compound expressed by general formula (2)



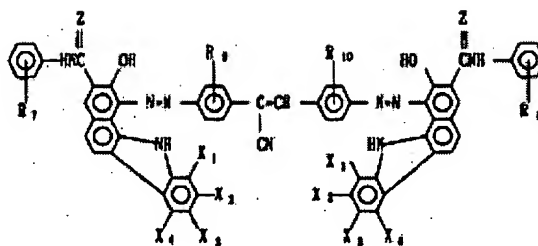
or

general formula (3)



(wherein  $R_3$  and  $R_4$  represent alkyl groups, aralkyl groups, aromatic rings or heterocyclic rings;  $R_5$  and  $R_6$  represent hydrogen atoms, alkyl groups, alkoxy groups or halogen atoms;  $Ar_3$  represents an aromatic rings or heterocyclic rings;  $Y$  represents a single bond,  $-CH_2-CH_2-$  or  $-CH=CH-$ ).

2. Electrophotographic photosensitive material according to Claim 1, wherein the charge-generating material is a disazo pigment expressed by general formula (4)



(wherein  $R_7$  and  $R_8$  represent alkyl groups, aralkyl groups, aromatic rings, alkoxy, halogen atoms, nitro groups, cyano groups or trifluoromethyl groups;  $R_9$  and  $R_{10}$  represent hydrogen atoms, alkyl groups, aralkyl groups, aromatic rings, alkoxy groups, halogen atom, cyano or trifluoromethyl;  $Z_1$ ,  $X_1$  [sic; Z],  $X_2$ ,  $X_3$  and  $X_4$  are the same as those in general formula (1)).

### Detailed explanation of the invention

#### Industrial application field

The present invention relates to an electrophotographic photosensitive material, more specifically to a lamination type electrophotographic photosensitive material having a charge generation layer containing a charge-generating material and a charge transport layer containing a charge-transporting material which receives carriers generated by the charge-generating material and transports them.

#### Prior art

As the organic photosensitive materials, electrophotographic photosensitive materials having photosensitive layers containing, as the principal component, a charge transfer complex formed from a photoconductive polymer represented by a poly-N-vinylcarbazole and a Lewis acid such as 2,4,7-trinitro-9-fluorenone, etc. have been put to practical use. However, these photosensitive materials are not necessarily satisfactory in terms of sensitivity and durability.

On the other hand, function separation type electrophotographic photosensitive materials, wherein the charge generation function and the charge transport function are allotted to different materials bring about notable improvement in sensitivity and durability, which are drawbacks in conventional organic photosensitive materials. These function separation type photosensitive materials have such advantages that the range of materials available as charge-generating material and charge-transporting material is wide and an electrophotographic photosensitive material having appropriate characteristics can be manufactured relatively easily. The function

separation type is suitable for setting a suitable range of spectral sensitivity for light emitting wavelengths of light sources as the electrophotographic photosensitive materials have been used especially in not only copiers but also in laser printers, LED printers, etc. in recent years.

As the charge-generating material, various azo pigments, phthalocyanine pigments, polycyclic quinone pigments, cyanine pigments, squaric acid dyes, pyrylium salt type pigments, etc. have been known. In azo pigments among them, many structures have been proposed from the viewpoints of strong lightfastness, large charge generating capacity, and easy material synthesis. As disazo pigments similar to the present invention, for example, Japanese Kokai Patent Application Nos. Sho 56[1981]-116040, Sho 57[1982]-182747, Sho 58[1983]-49952, Sho 58[1983]-115447, Sho 59[1984]-72448, Sho 59[1984]-155848, Sho 58[1983]-115445, Sho 58[1983]-115446, and Sho 59[1984]-7365 are already known. The following requirements for azo pigments to be used as the charge-generating material may be mentioned: (i) it should be stable against heat and light, (ii) in the case of those showing the charge generation function in dispersed state, they should easily disperse and the change in dispersion over time should be small, (iii) the charge generation function should not change due to temperature, (iv) the characteristics should not change in repeated use, (v) they should have effective spectral sensitivity with respect to the light source used, and (vi) the charge-transporting material should not be limited. It is most important in practical use that these requirements are, on average, at a satisfactorily high level. Some of the aforementioned known pigments satisfy part of the above requirements, but none satisfy these requirements at a high level.

On the other hand, as the charge-transporting material, hydrazone compounds, pyrazoline compounds, stilbene compounds, triarylmethane compounds, arylamine compounds, etc. are known. The following requirements for these compounds, may be mentioned: (i) they should be stable against light and heat, (ii) they should be stable against ozone generated by corona discharge, NO<sub>x</sub>, nitric acid, etc., (iii) they should display a high transport function, and (iv) the miscibility with organic solvent binders should be high.

Combinations of the aforementioned known azo pigments and charge-transporting materials include those in: Japanese Kokai Patent Application Nos. Sho 58[1983]-18636, Sho 57[1982]-204551, Sho 59[1984]-44050, Sho 59[1984]-44051, Sho 59-157644, Sho 60[1985]-24549, Sho 60[1985]-24550, Sho 60[1985]-24551, and Sho 60[1985]-24552, etc.

Photosensitive materials of the above combination have low fluctuation in potential in repeated use, but many of them have large drawbacks in image characteristics such as deterioration of image by change of application environment so that they cause problems in practical use.

#### Problem to be solved by the invention

The purpose of the present invention is to provide electrophotographic photosensitive materials which have high sensitivity, maintain stable potential in repeated use and show stable sensitivity and image characteristics regardless of the application environment (temperature, humidity) in function separation type photosensitive materials having a charge generation layer and a charge transport layer.

In addition, the purpose of the present invention is to provide azo pigments which are easily dispersed to obtain a dispersion showing little change over time.

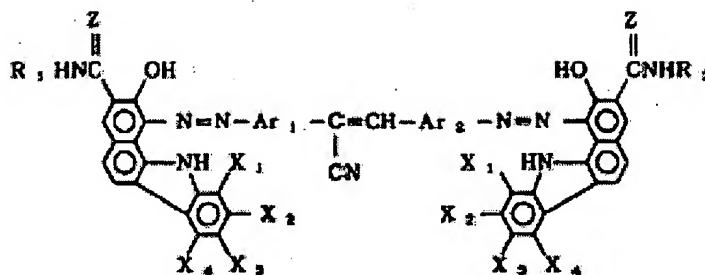
In addition, the purpose of the present invention is to provide electrophotographic photosensitive materials showing sufficiently high sensitivity against light sources in the region of 600-700 nm.

In addition, the purpose of the present invention is to provide photosensitive materials stable against ozone generated by corona discharge, NO<sub>x</sub>, nitric acid, etc.

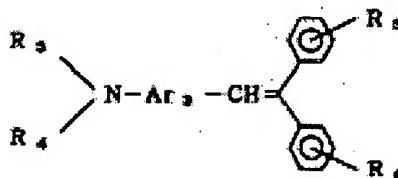
#### Means to solve the problems

The present inventors found as a result of their study that a lamination type electrophotographic photosensitive material having a charge generation layer containing a disazo pigment of specific structure and a charge transport layer containing a styryl compound of specific structure solves the aforementioned problem and displays superior electrophotographic characteristics.

Namely, the present invention is an electrophotographic photosensitive material, characterized in that in a lamination type electrophotographic photosensitive material having a charge generation layer and a charge transport layer on a substrate, the charge generation layer contains, as the charge-generating material, a disazo pigment expressed by general formula (1)

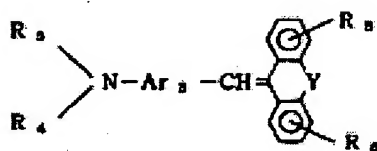


and the charge transport layer contains, as the charge-transporting material, a styryl compound expressed by general formula (2)



or

general formula (3)



In general formula (1),  $R_1$  and  $R_2$  represent alkyl groups, aralkyl groups, aromatic rings or heterocyclic rings, and concretely alkyl groups such as methyl, propyl, butyl, etc., aralkyl groups such as benzyl, phenethyl, naphthylmethyl, etc., aromatic rings such as phenyl, diphenyl, naphthyl, anthryl, etc., and heterocyclic rings such as carbazole, dibenzofuran, benzimidazolone, benzothiazole, thiazole, pyridine, etc. are exemplified.

In addition, these alkyl groups, aralkyl groups, aromatic ring and heterocyclic ring may have substitution groups such as alkyl groups, e.g., methyl, ethyl, propyl, etc., alkoxy groups, e.g. methoxy, ethoxy, propoxy, etc., halogen groups, e.g., fluorine, chlorine, bromine, etc., or nitro groups, cyano groups, trifluoromethyl groups, etc.  $Ar_1$  and  $Ar_2$  represent aromatic rings or heterocyclic rings, and concrete examples of these aromatic rings and heterocyclic rings are the same as above. In addition, these aromatic rings and heterocyclic rings may have substitution

groups, as mentioned above such as, alkyl groups, alkoxy groups, halogen atoms or cyano groups.

$X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  represent hydrogen atoms, alkyl groups, alkoxy groups, halogen atoms, nitro groups, cyano groups or trifluoromethyl groups, as long as they do not all represent hydrogen.

Z represents an oxygen or sulfur atom.

$R_3$  and  $R_4$  in general formula (2) and general formula (4) represent alkyl groups, aralkyl groups, aromatic rings or heterocyclic rings, concretely represent alkyl groups such as methyl, ethyl, propyl, butyl, etc., aralkyl groups such as benzyl, phenethyl, naphthylmethyl, etc., aromatic rings such as phenyl, diphenyl, naphthyl, anthryl, etc. or heterocyclic rings such as pyridyl, quinolyl, thienyl, furyl, etc. In addition, these alkyl groups, aralkyl groups, aromatic rings and heterocyclic rings may have substitution groups, for example, alkyl groups such as methyl, ethyl, propyl, etc., alkoxy groups such as methoxy, ethoxy, propoxy, etc., halogen such as fluorine, chlorine, bromine, etc. and nitro groups.

$R_5$  and  $R_6$  represent hydrogen atoms, alkyl groups, alkoxy groups or halogen atoms. Concrete examples of  $R_5$  and  $R_6$  are the same as above. In addition, the alkyl and alkoxy groups may have substitution groups as mentioned above.

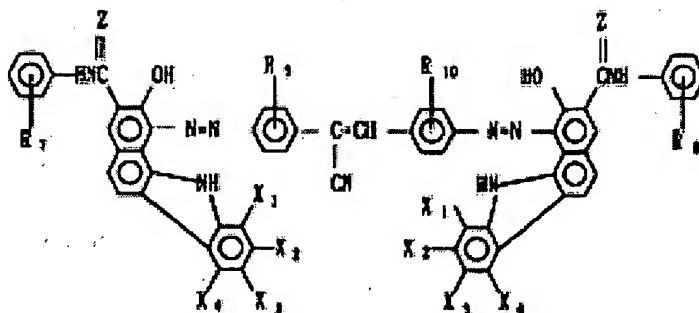
$Ar_3$  represents an aromatic rings or heterocyclic rings, and concretely it represents an aromatic rings such as phenyl, naphthyl, etc. or heterocyclic rings such as pyridyl, quinolyl, thienyl, furyl, etc. The aromatic rings and heterocyclic rings may have substitution group. Substitution groups for  $Ar_3$  include alkyl groups such as methyl, ethyl, propyl, etc., alkoxy groups such methoxy, ethoxy, propoxy, etc., halogen atoms such as fluorine, chlorine, bromine, etc. or nitro groups.

Y in the general formula (3) represents a single bond,  $-CH_2CH_2-$  or  $-CH=CH-$ .

Furthermore, the disazo pigment having a structure expressed by general formula (4) among the aforementioned charge-generating materials is especially superior in electrophotographic characteristics.

General formula (4)





In general formula (4),  $R_7$  and  $R_8$  represent hydrogen atoms, alkyl groups such as methyl, ethyl, propyl, etc., aralkyl groups such as benzyl, phenetyl, naphthylmethyl, etc., aromatic rings such as phenyl, naphthyl, anthranyl, etc., alkoxy groups such as methoxy, ethoxy, propoxy, etc., halogen atoms such as fluorine, chlorine, bromine, etc., nitro groups, cyano groups or trifluoromethyl groups.

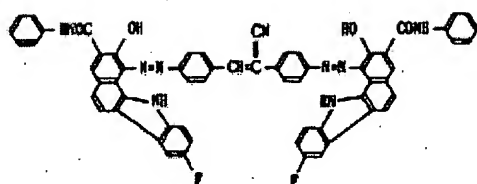
$R_9$  and  $R_{10}$  represent hydrogen atoms, alkyl groups such as methyl, ethyl, propyl, etc., aralkyl groups such as benzyl, phenetyl, naphthylmethyl, etc., aromatic rings such as phenyl, naphthyl, anthranyl, etc., alkoxy groups such as methoxy, ethoxy, propoxy, etc., halogen atoms such as fluorine, chlorine, bromine, etc., cyano groups or nitro groups. The alkyl groups, aromatic rings, aralkyl groups and alkoxy groups of  $R_7$ ,  $R_8$ ,  $R_9$  and  $R_{10}$  may have substitution groups, for example, alkyl groups such as methyl, ethyl, propyl, etc., alkoxy groups such as methoxy, ethoxy, propoxy, etc., halogen atoms such as fluorine, chlorine, bromine, etc., nitro groups, cyano groups and trifluoromethyl groups.

$Z$ ,  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  have the same meaning as those for general formula (1).

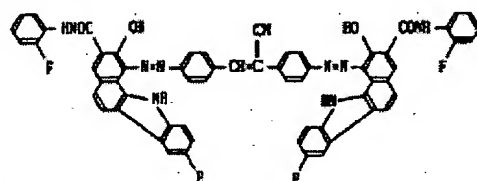
Next, typical examples of charge-generating materials and charge-transporting materials to be used in the present invention are exemplified.

Charge-generating materials

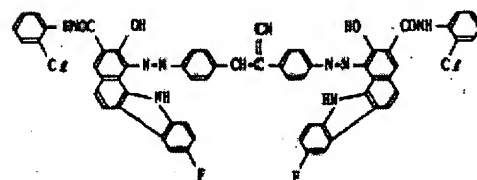
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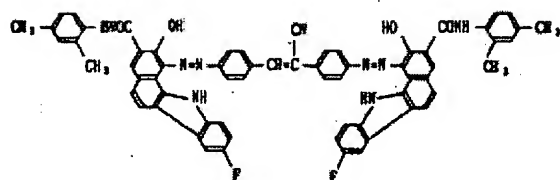
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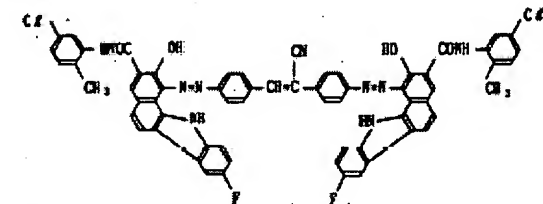
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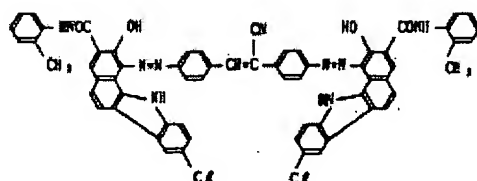
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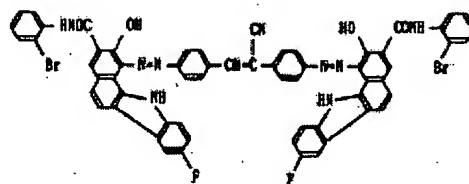
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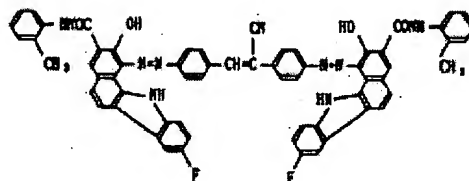
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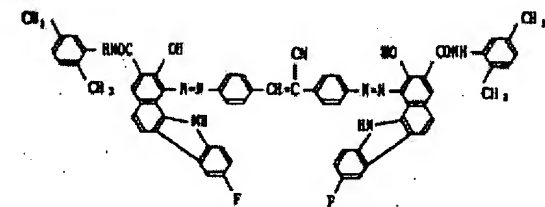
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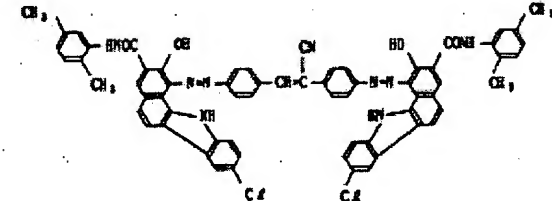
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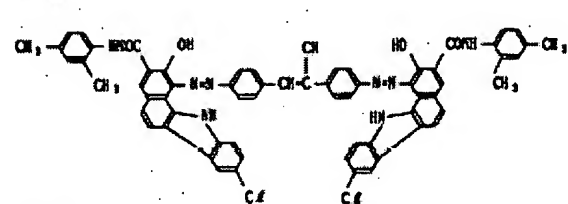
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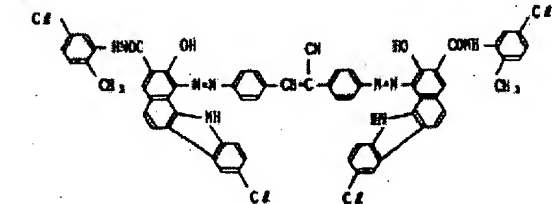
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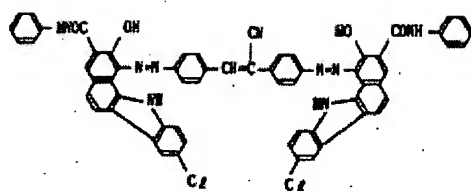
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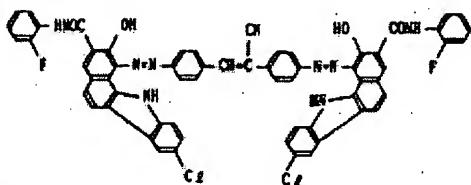
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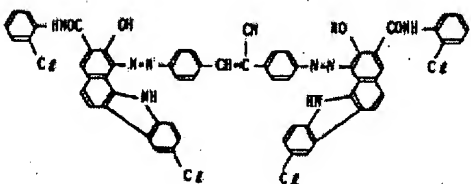
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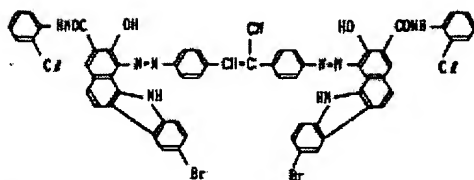
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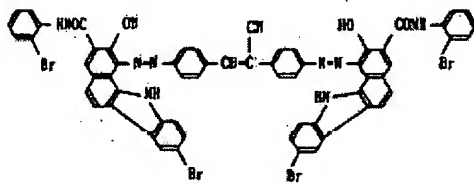
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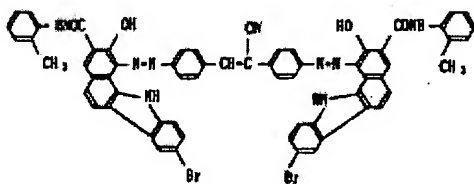
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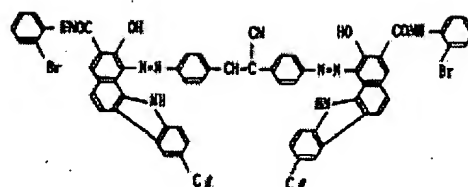
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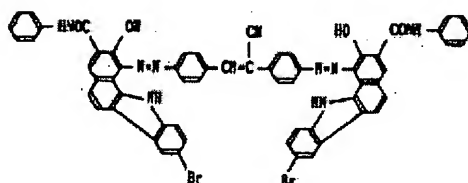
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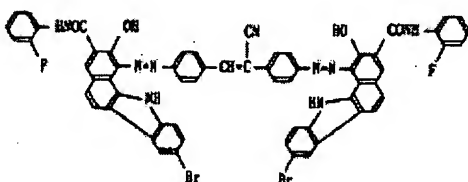
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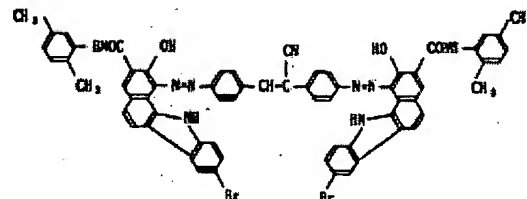
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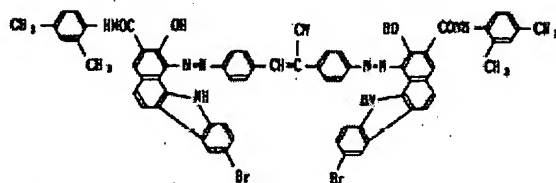
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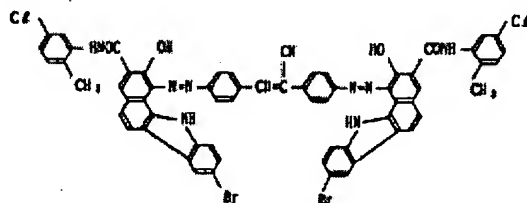
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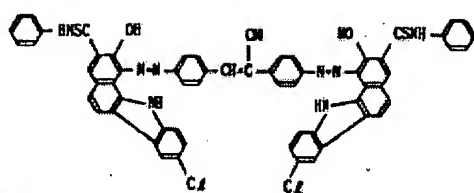
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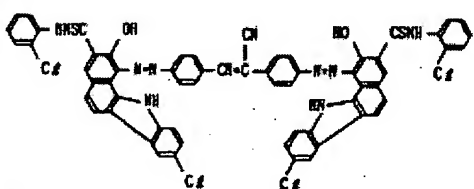
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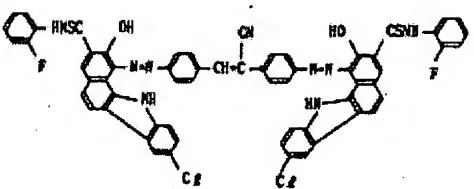
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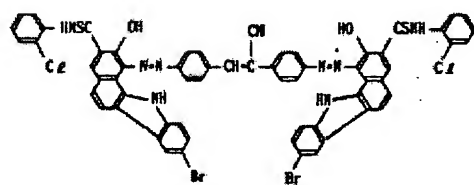
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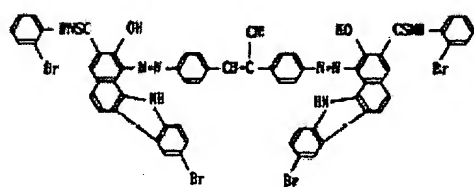
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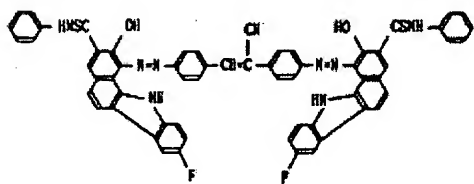
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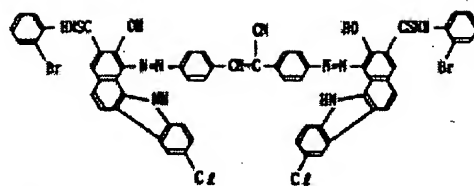
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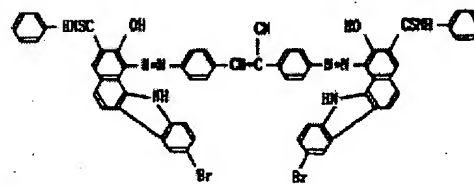
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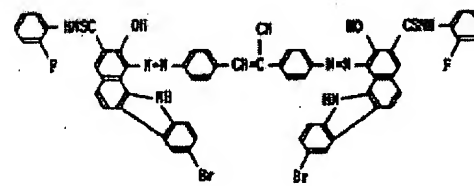
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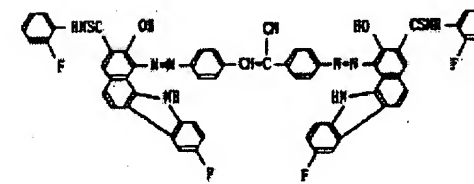
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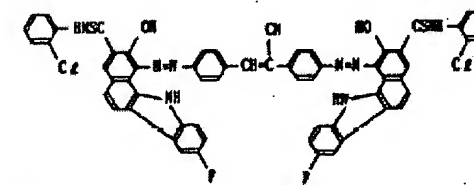
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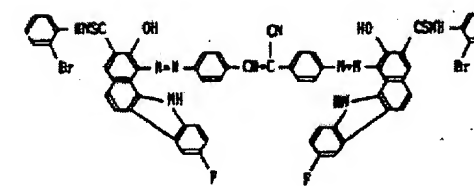
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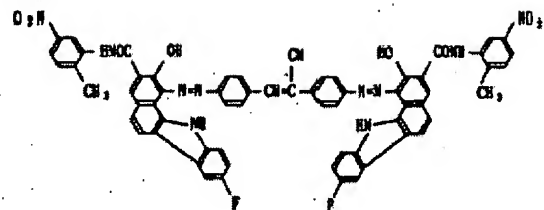
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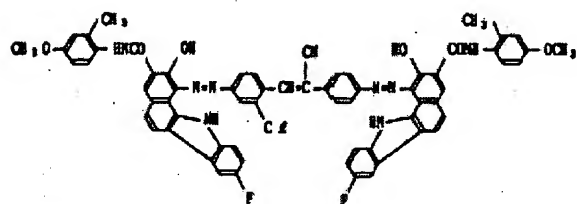
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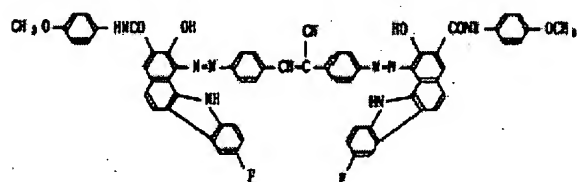
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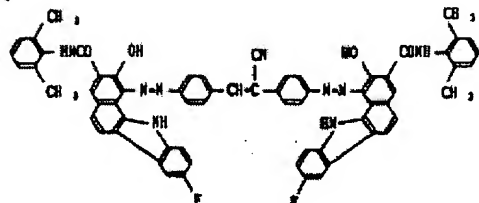
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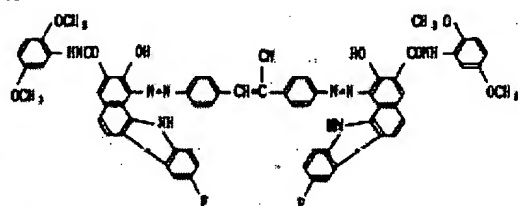
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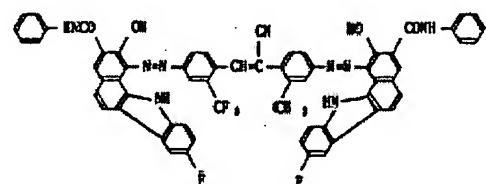
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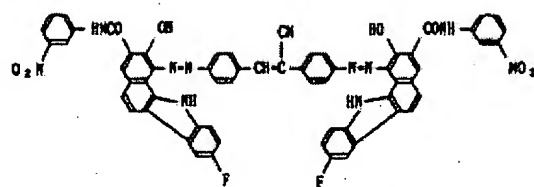
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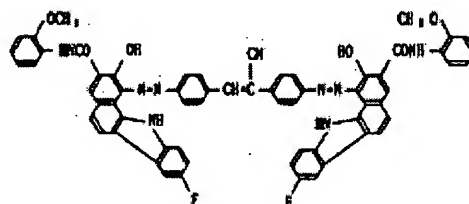
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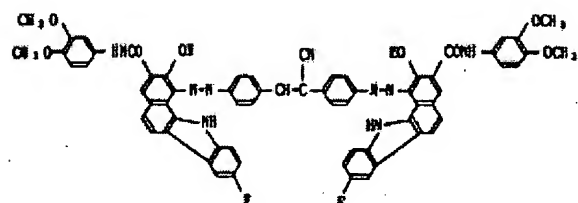
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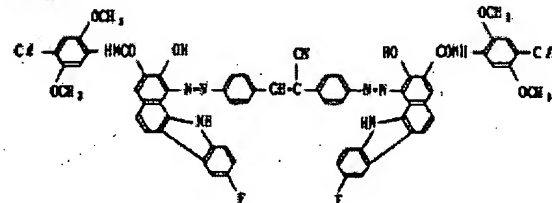
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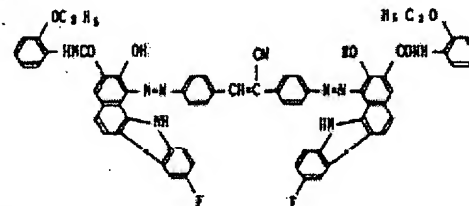
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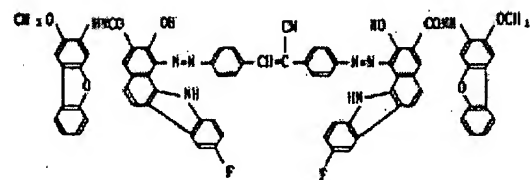
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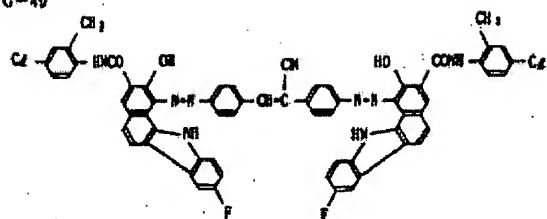
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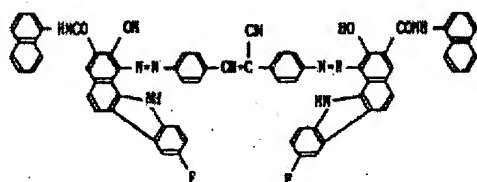
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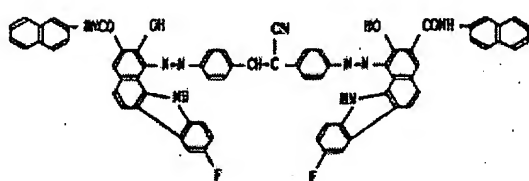
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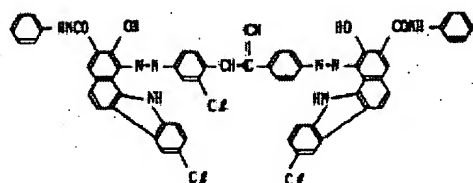
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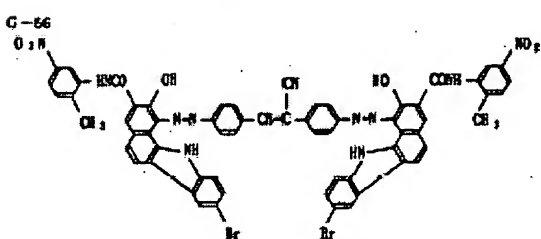
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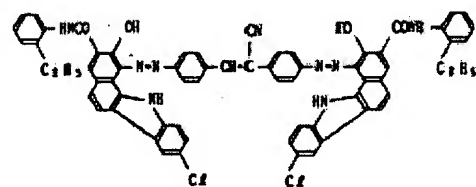
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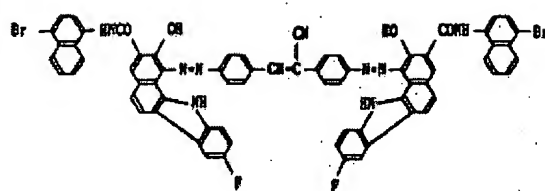
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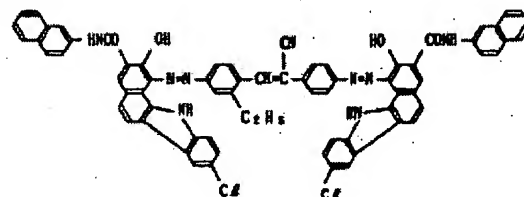
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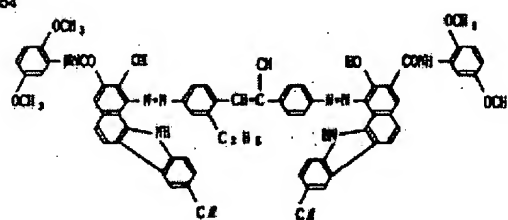
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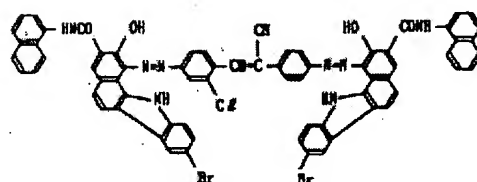
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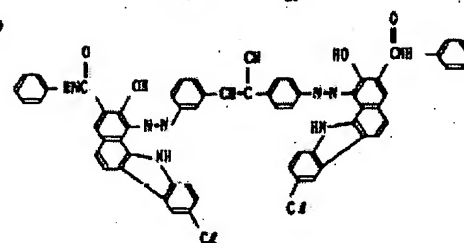
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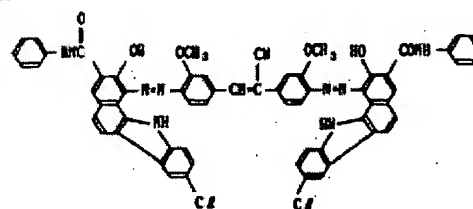
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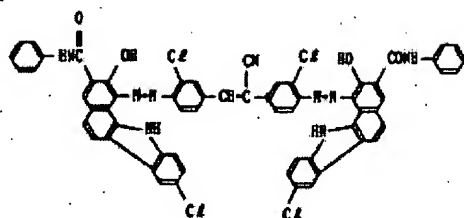
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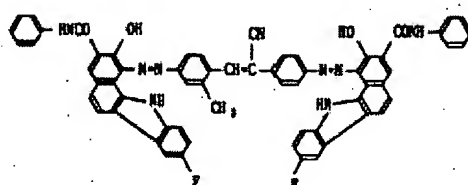
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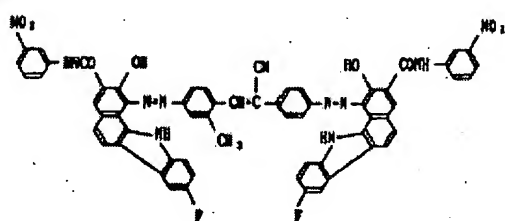
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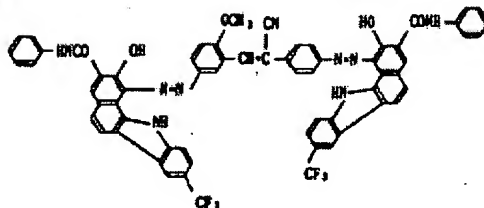
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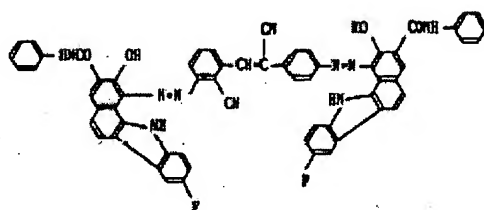
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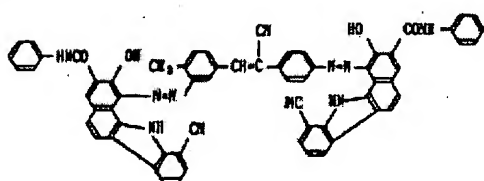
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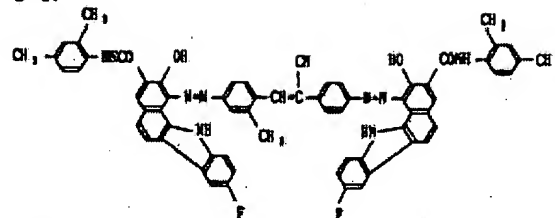
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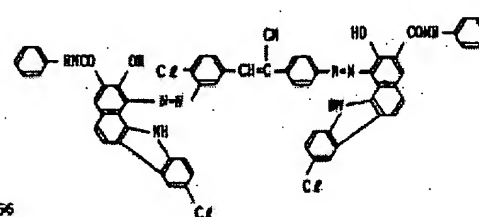
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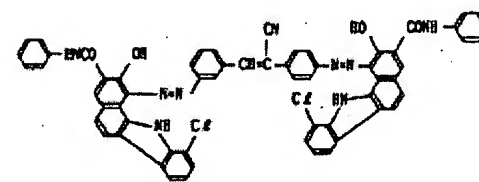
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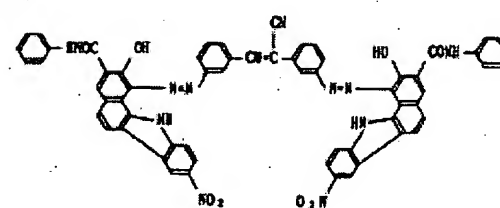
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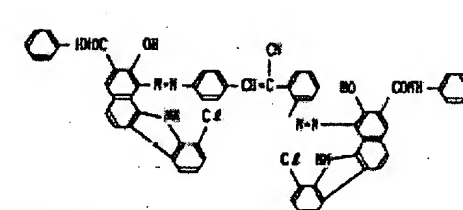
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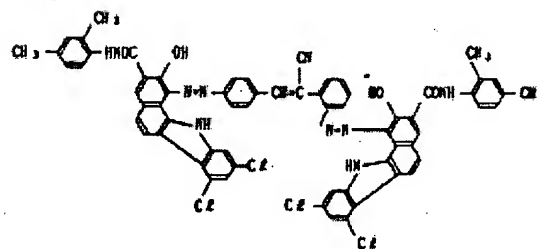
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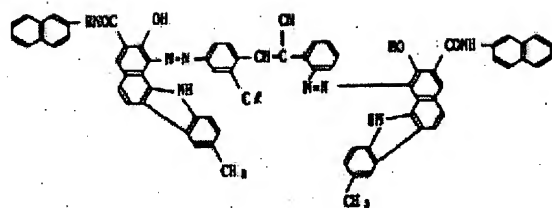
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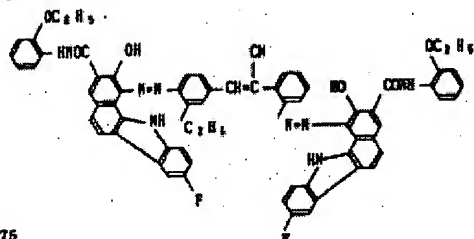
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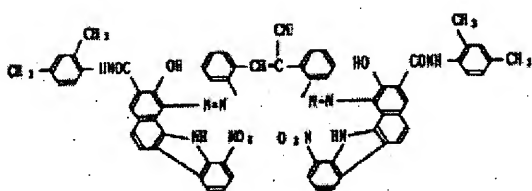
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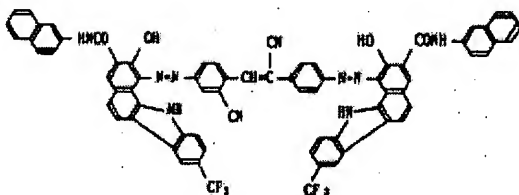
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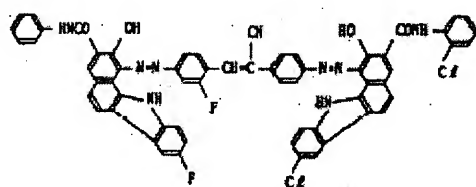
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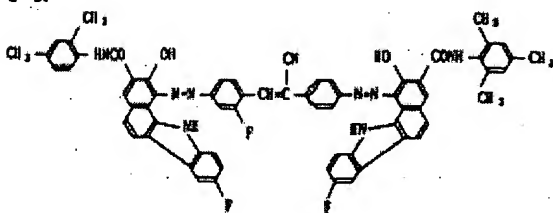
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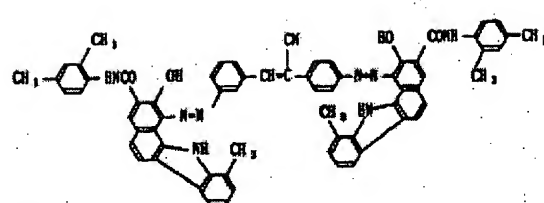
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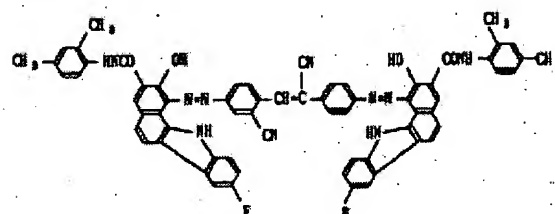
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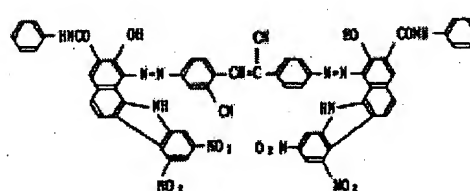
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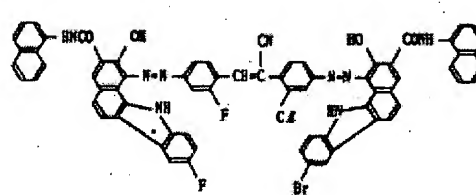
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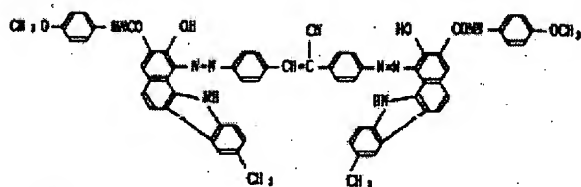
G-78



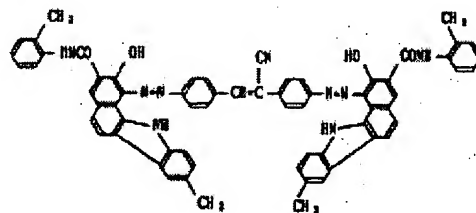
G-82



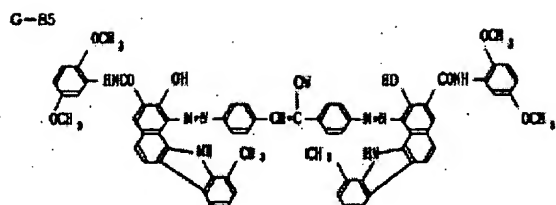
G-83



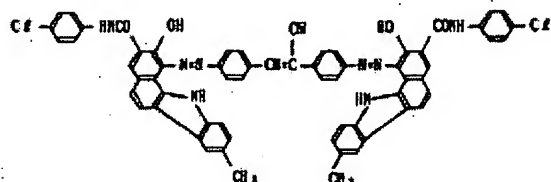
G-84



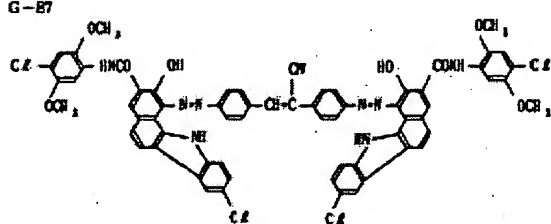




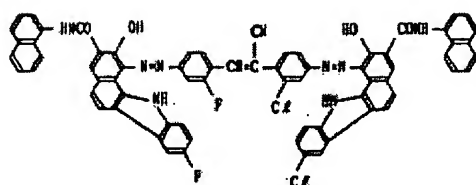
G-86



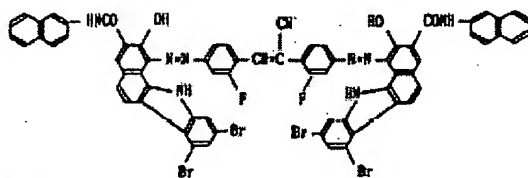
G-87



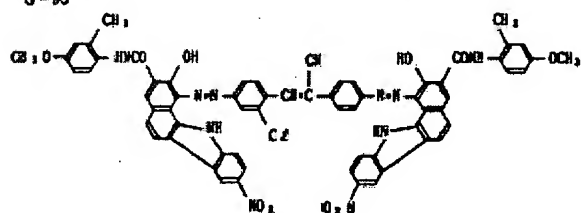
G-91



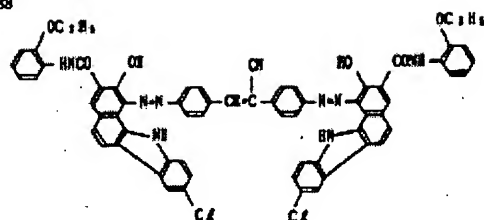
G-92



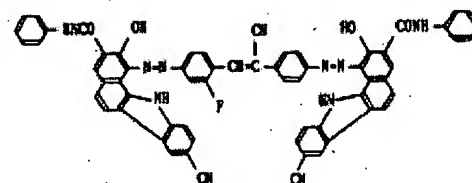
G-93



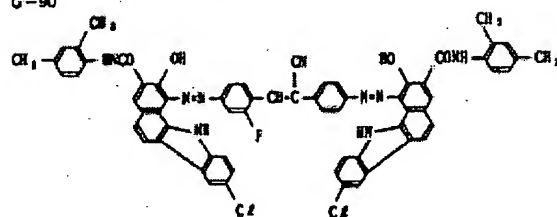
G-88



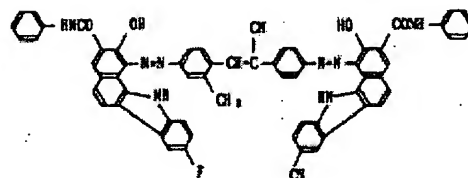
G-89



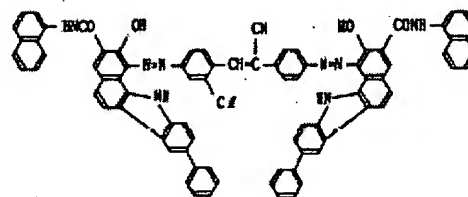
G-90



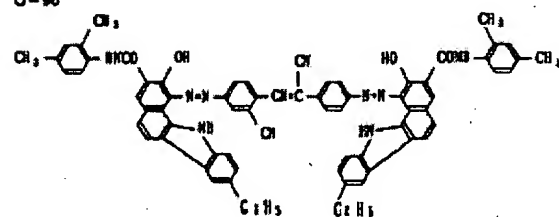
G-94



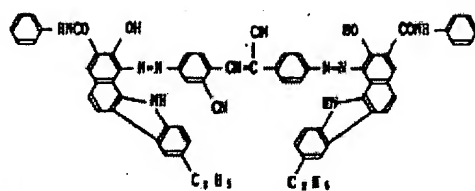
G-95



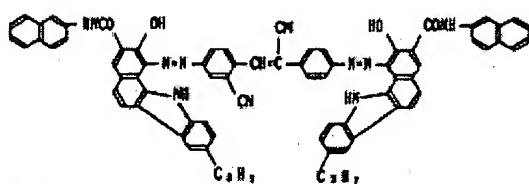
G-96



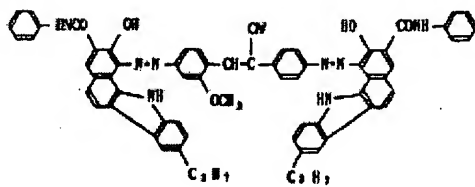
G-97



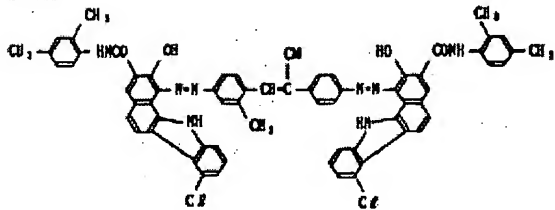
G-98



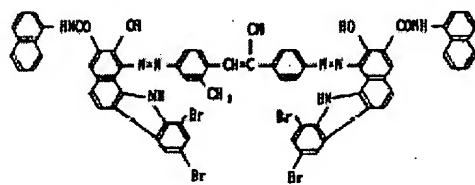
G-99



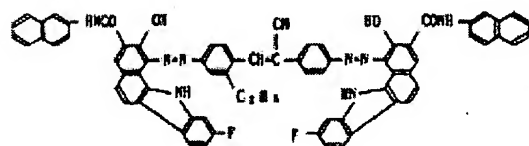
G-103



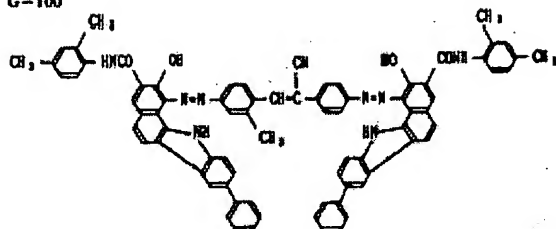
G-104



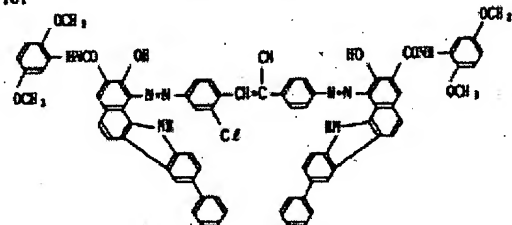
G-105



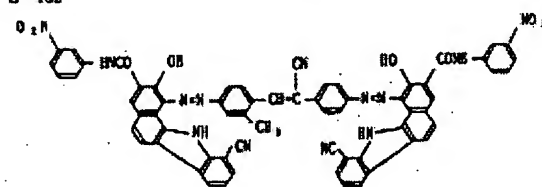
G-100



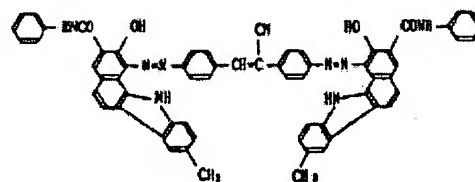
G-101



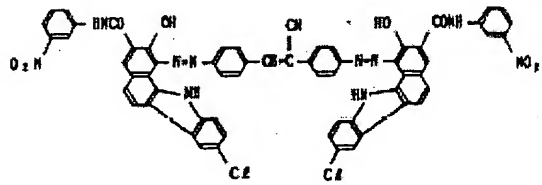
G-102



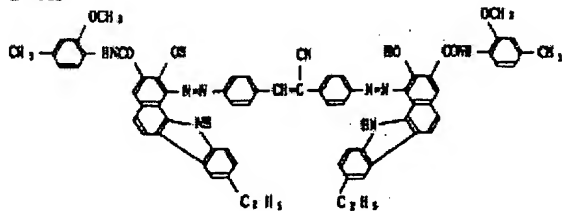
G-106



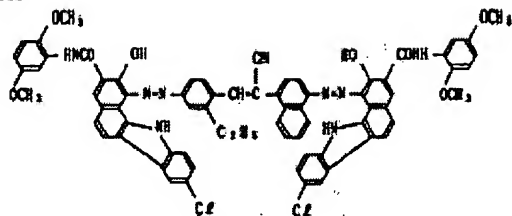
G-107



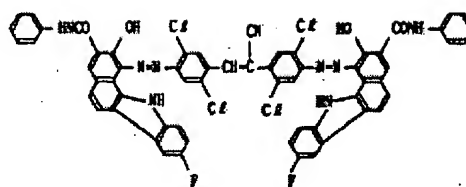
G-108



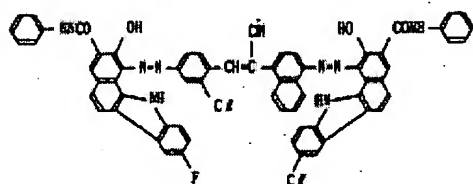
G-109



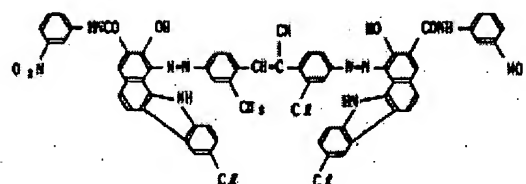
G-112



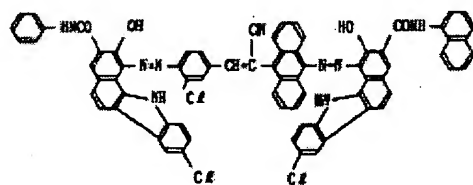
G-110



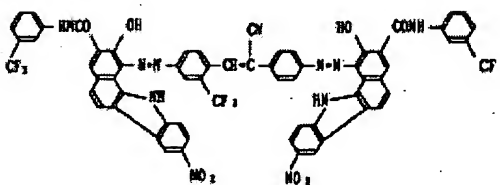
G-113



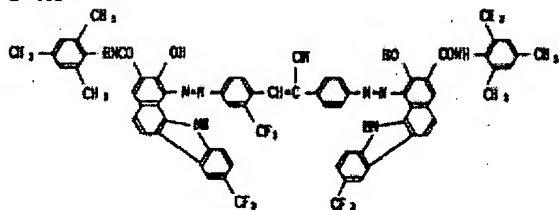
G-111



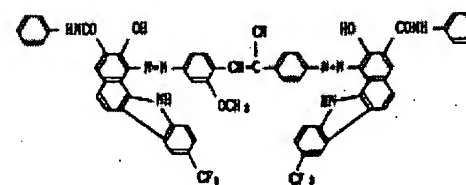
G-114



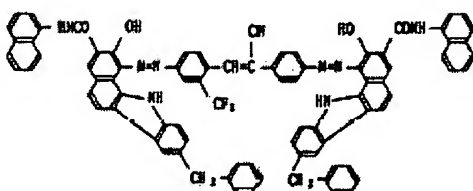
G-115



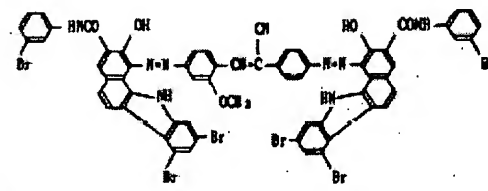
G-118



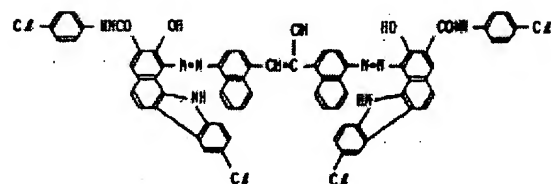
G-116



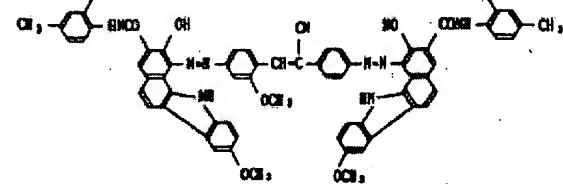
G-119



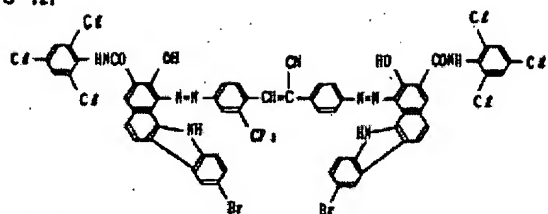
G-117



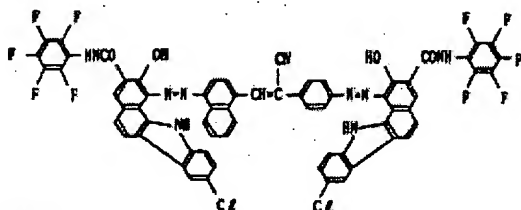
G-120



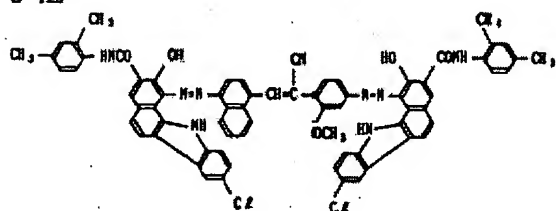
G-121



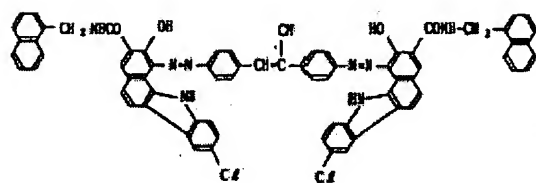
G-122



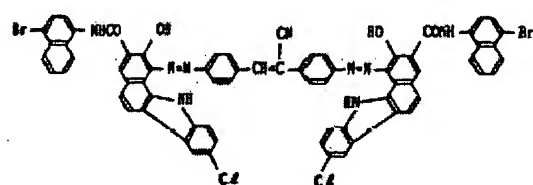
G-123



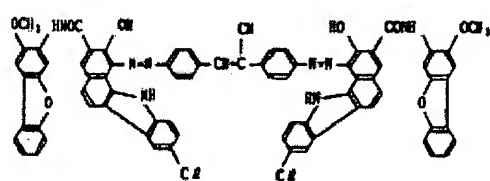
G-127



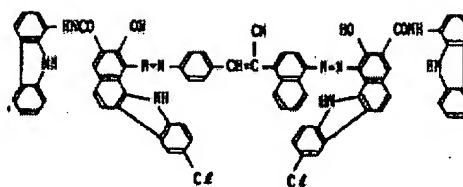
G-128



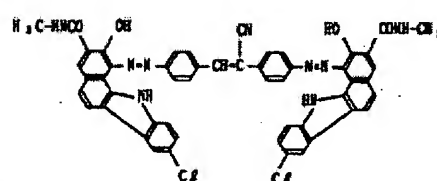
G-129



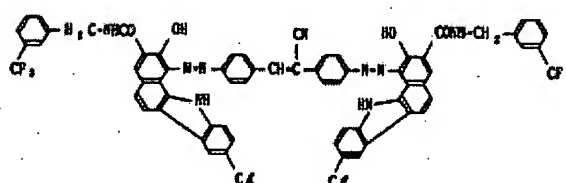
G-124



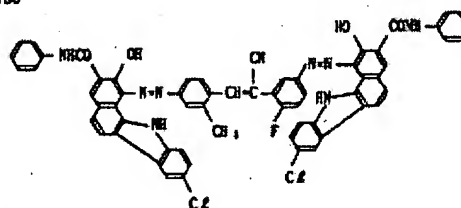
G-125



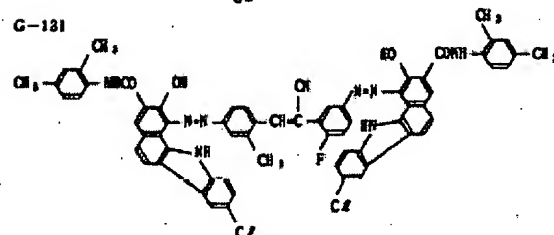
G-126



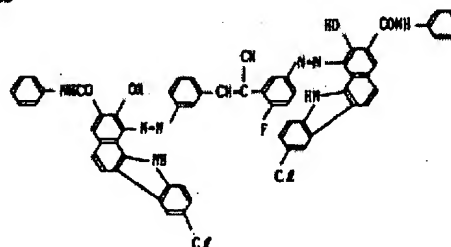
G-130



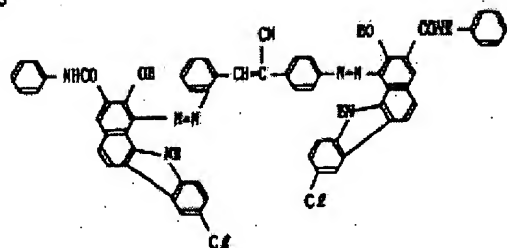
G-131



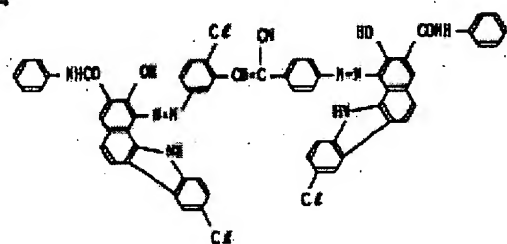
G-132



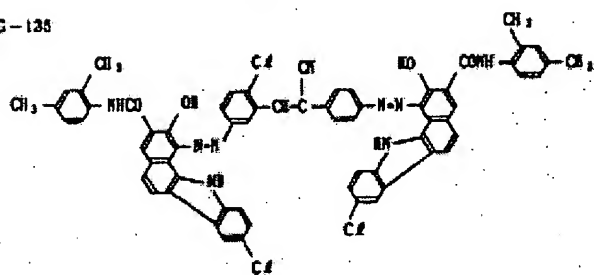
G-133



G-134

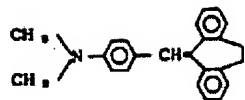


G-135

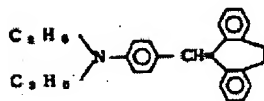


Charge-transporting materials

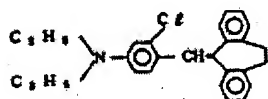
T-1



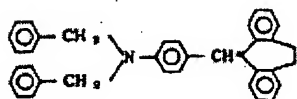
T-2



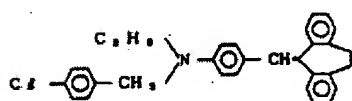
T-3



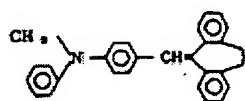
T-4



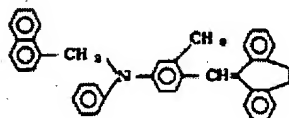
T-5



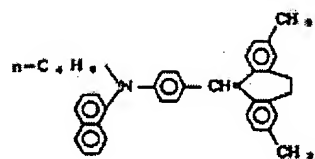
T-6



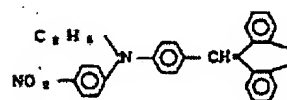
T-7



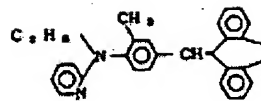
T-8



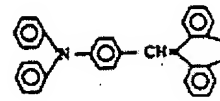
T-9



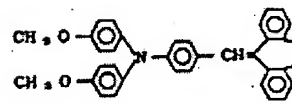
T-10



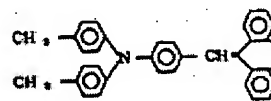
T-11



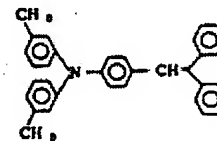
T-12



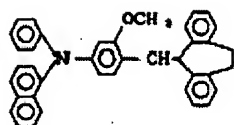
T-13



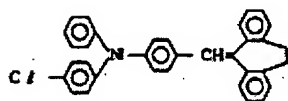
T-14



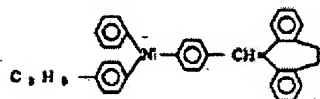
T-15



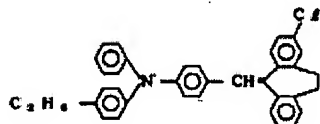
T-16



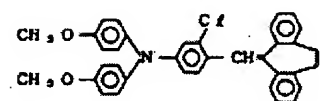
T-17



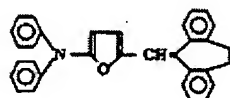
T-18



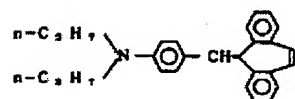
T-19



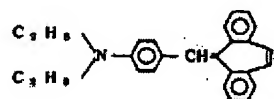
T-25



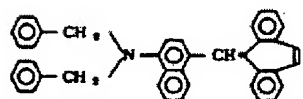
T-26



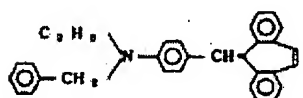
T-27



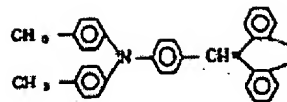
T-28



T-29



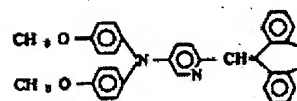
T-20



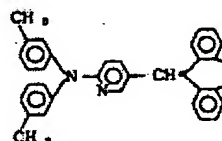
T-21



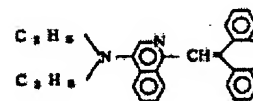
T-22



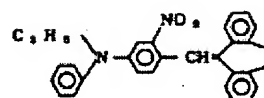
T-23



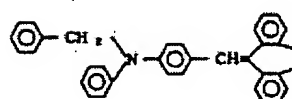
T-24



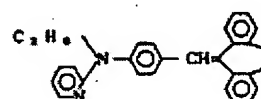
T-30



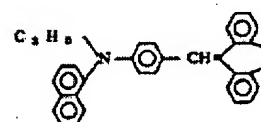
T-31



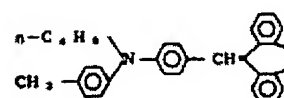
T-32



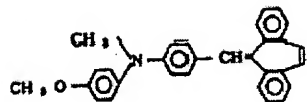
T-33



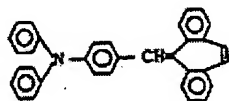
T-34



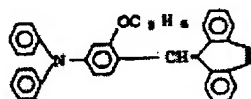
T-35



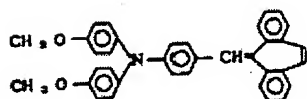
T-36



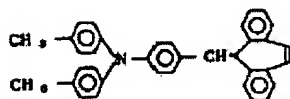
T-37



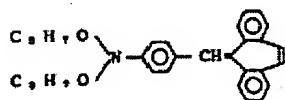
T-38



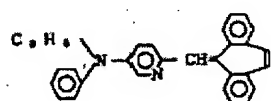
T-39



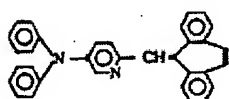
T-45



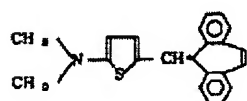
T-46



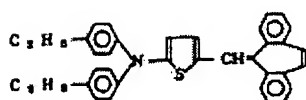
T-47



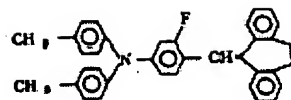
T-48



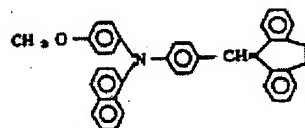
T-49



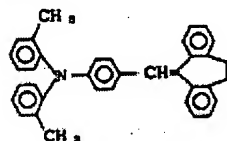
T-40



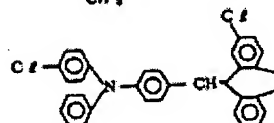
T-41



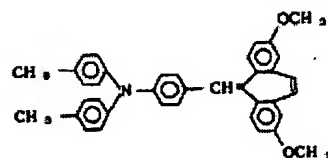
T-42



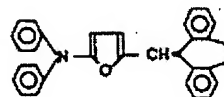
T-43



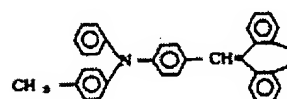
T-44



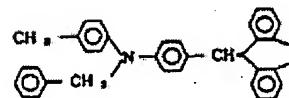
T-50



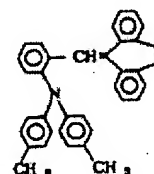
T-51



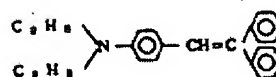
T-52



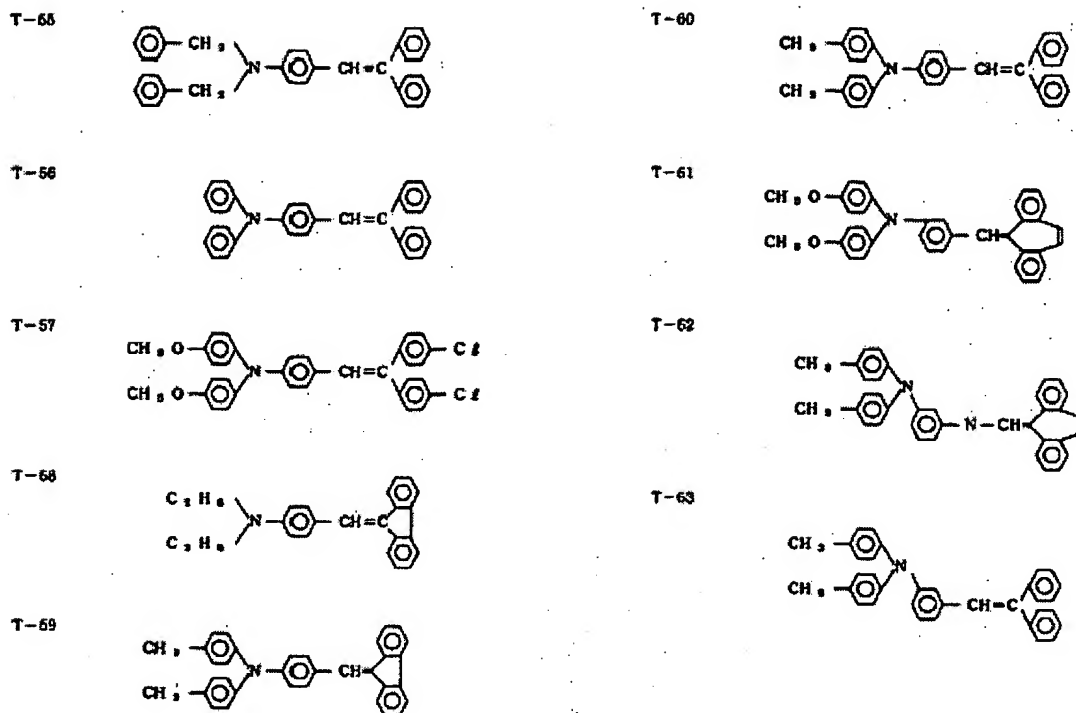
T-53



T-54







Hereinafter, the electrophotographic photosensitive material of the present invention is explained using a figure.

Figure 1 shows schematically the layer constitution of an electrophotographic photosensitive material of the present invention.

It is preferred that the charge generation layer 2 containing disazo pigment expressed by general formula (1) contain as much of the aforementioned photoconductive compound as possible to obtain sufficient absorbance and it is made into a thin layer of, for example, 5  $\mu\text{m}$  or less, preferably 0.01  $\mu\text{m}$  to 1  $\mu\text{m}$  in order to shorten the range of generated charge carriers.

The charge generation layer can be formed by dispersing the aforementioned disazo pigment in a suitable binder and coating it on a support or it can be obtained by forming a vapor deposition film using a vacuum vapor deposition device. The binder for forming the charge generation layer by coating can be selected from a wide range of insulating resins, or can be selected from organic photoconductive polymers such as poly(N-vinylcarbazole), polyvinylanthracene, polyvinylpyrene, etc. Preferably, insulating resins such as polyvinylbutyral, polyarylates (condensation polymers of bisphenol A and phthalic acid, etc.), polycarbonate, polyester, phenoxy resin, polyvinyl acetate, acrylic resin, polyacrylamide resin, polyamide, polyvinylpyridine, cellulose resins, urethane resins, epoxy resins, casein, polyvinyl alcohol,

polypyrrolidone, etc. may be exemplified. The content of resins in the charge generation layer is 80% by weight or less, preferably 40% by weight or less.

Solvents for dissolving these resins vary with the type of resin, and it is preferred to select those which do not dissolve in the charge transport layer or the subbing layer. Concretely, as the organic solvents, alcohols such as methanol, ethanol, isopropanol, etc., ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc., amides such as N,N-dimethylformamide, N,N-dimethylacetamide, etc., sulfoxides such as dimethyl sulfoxide, etc., ethers such as tetrahydrofuran, dioxane, ethylene glycol monomethyl ether, etc., aliphatic halohydrocarbons such as chloroform, methylene chloride, dichloroethylene, carbon tetrachloride, trichloroethylene, etc., and aromatics such as benzene, toluene, xylene, ligroin, monochlorobenzene, dichlorobenzene, etc. can be used.

Coating can be carried out by using coating processes such as immersion coating, spray coating, Meyer bar coating, blade coating, etc. Drying method of heating after drying at room temperature until tack free is preferred. The drying by heating can be carried out by heating at 30-200°C for 5 min to 2 h stationary or in an air flow.

The charge transport layer 3 is connected electrically to the charge generation layer 2 and has the function of receiving charge carriers injected from the charge generation layer under the presence of an electric field and transporting the charge carriers to the surface. In this case, it is preferred to laminate the charge transport layer 3 on the upper surface of the charge generation layer 2, but the charge transport layer 3 may be laminated on the bottom surface of the charge generation layer 2.

The charge transport layer 3 can be formed by dissolving the aforementioned charge-transporting material in a suitable binder and coating. As resins which may be used as binder, for example, insulating resins such as acrylic resin, polyarylate, polyester, polycarbonate, polystyrene, acrylonitrile-styrene copolymer, acrylonitrile-butadiene copolymer, polyvinylbutyral, polyvinylformal, polysulfone, polyacrylamide, polyamide, chlorinated rubber, etc., or organic photoconductive polymers such as poly(N-vinylcarbazole), polyvinylanthracene, polyvinylpyrene, etc. can be exemplified.

The charge transport layer 3 may not exceed a certain thickness since there is a limit in transport of the charge carriers. The thickness is generally 5-35  $\mu\text{m}$  and preferably 8-30  $\mu\text{m}$ . In

the formation of the charge transport layer by coating, a suitable coating process can be used as mentioned above.

The photosensitive material layer 4 having a lamination structure of the charge generation layer 2 and the charge transport layer 3 is formed on an electrically conductive support 1. As the electrically conductive support 1, a support having electric conductivity, for example, aluminum, aluminum alloy, stainless steel, etc. can be used. In additions, plastics having a coating layer formed from aluminum, aluminum alloy, indium oxide, tin oxide, indium oxide-tin oxide alloy, etc. by vacuum vapor deposition, plastic support or metallic support coated with a mixture of electrically conductive particles (for example, carbon black, silver particles, etc.) and a suitable binder, support obtained by impregnating electrically conductive particle in plastic or paper, and plastics containing an electrically conductive polymer can be used.

A subbing layer having a barrier function and adhesion function can be installed between the electric conductive support 1 and the photosensitive material 4. The subbing layer can be formed from casein, polyvinyl alcohol, nitrocellulose, ethylene-acrylic acid copolymer, polyamide (nylon 6, nylon 66, nylon 610, copolymerized nylon, alkoxymethylated nylon, etc.), polyurethane, gelatin, aluminum oxide, etc.

The thickness of the subbing layer is 0.1-5  $\mu\text{m}$ , preferably 0.5-3  $\mu\text{m}$ .

The electrophotographic photosensitive material of the present invention can be utilized not only in electrophotographic copiers but also in other electrophotography application fields such as laser printers, LED printers, liquid crystal printers, laser photoengravings, etc. Its efficiency is especially apparent in LED printers.

#### Application examples

Hereinafter, the preset invention is explained with application examples.

##### Application Example 1

A subbing layer of 0.1  $\mu\text{m}$  was formed from vinyl chloride-maleic anhydride-vinyl acetate copolymer on an aluminum plate.

Then, 5 g of the above illustrated disazo pigment (G-13) were dissolved in a solution obtained by dissolving 2 g of butyral resin (butyralization 63 mol%, number-average molecular weight 20,000) in 95 mL of cyclohexanone and dispersed 20 h in a sand mill. The dispersion was

coated at a dry thickness of 0.5  $\mu\text{m}$  on the subbing layer with a Meyer bar and dried to form a charge generation layer.

Next, 5 g of the above illustrated styryl compound (T-39) and 5 g of bisphenol Z type polycarbonate resin (viscosity-average molecular weight 30,000) were dissolved in 70 mL of chlorobenzene, and it was coated at a dry thickness of 22  $\mu\text{m}$  on the charge generation layer with a Meyer bar and dried to form a charge transport layer to obtain Photosensitive Material No. 1.

The electrophotographic photosensitive material thus obtained was corona charged to -5.5 kV by the static method using electrostatic copying paper testing device Model SP-428, Kawaguchi Denki, K.K., kept in a dark place for 1 h, and exposed to a halogen lamp with a luminance of 2 lux and its electrification characteristics were examined. As the electrification characteristics, the exposure amount ( $E_{1/2}$ ) necessary for decay of the surface potential ( $V_0$ ) and potential ( $V_D$ ) in 1 sec of dark decay of the surface potential to 1/2 was measured.

The results are shown below.

$$V_0: -720 \text{ V}$$

$$V_D: -700 \text{ V}$$

$$E_{1/2}: 0.99 \text{ lux}\cdot\text{sec}$$

Next, the spectral intensity was measured using monochromatic light of light intensity 1  $\mu\text{W}/\text{cm}^2$  as the light source in the electrostatic copying paper testing device. For the sensitivity, the exposure amount  $E_{\Delta 500\text{V}}$  ( $\mu\text{J}/\text{cm}^2$ ) required for the surface potential to reach -200 V in the case of a surface potential ( $V_D$ ) of -700 V was measured, and

$$E (\text{V}\cdot\text{cm}^2/\mu\text{J}) = 500 (\text{V}) / E_{\Delta 500\text{V}} (\mu\text{J}/\text{cm}^2)$$

was calculated plotted with respect to the wavelength in Figure 2.

Furthermore, the photosensitive material was applied to the cylinder of the electrophotographic copying machine provided with a -5.6 kV corona discharger, exposure optical system, developer, transfer charger, charge removing exposure optical system and cleaner, and the image characteristics were examined. In the copying machine, images were obtained on the transfer paper accompanied with driving of the cylinder. The evaluation of the image characteristics using the copier was carried out in three environments of humidity 10% and temperature 5°C, humidity 50% and temperature 18°C, and humidity 80% and temperature 35°C. Complete, satisfactory images of the original were obtained in all environments. It was

found that the photosensitive material showed satisfactory image characteristics without showing spotting, fuzziness, etc. even at the 10,000th copy.

### Application Example 2

Photosensitive materials were manufactured in the same manner as in Application Example 1 except that disazo pigment (G-13) of Application Example 1 was replaced with disazo dyes G-10, G-11, G-19 and G-14, and their electrification characteristics and spectral sensitivity were measured. The electrification characteristics are shown in Table 1, and the spectral sensitivity is shown in Figure 3.

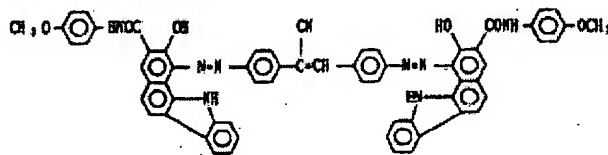
Table 1

① 実験例	② 感光体 No.	③ ジアゾ染料	$V_0$ (V)	$V_D$ (V)	$E_k$ ( $\mu\text{ux} \cdot \text{sec}$ )
2	2	G-10	-720	-690	1.34
3	3	G-11	-740	-704	2.11
4	4	G-14	-700	-650	1.55
5	5	G-19	-700	-680	0.90

Key: 1      Application example  
 2      Photosensitive material  
 3      Disazo pigment

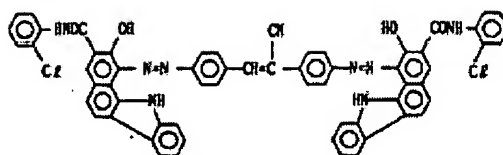
### Comparative Examples 1 and 2

A photosensitive material as Comparative Example 1 disclosed in Japanese Kokai Patent Application No. Sho 59[1984]-157644 was manufactured in the same manner as in Application Example 1 except that comparative disazo pigment (1) shown below was used, and its electrification characteristics were examined in the same way as in Application Example 1.



Comparative pigment (1)

Furthermore the same evaluation was also conducted on comparative pigment (2) with the following structure.



Comparative pigment (2)

The results are shown in Table 2.

Table 2

① 比較例	② 比較感光材料	③ 比較顔料	$V_D$ (V)	$V_D$ (V)	ES (lux · sec)
1	1	1	-730	-720	7.06
2	2	2	-720	-700	3.90

Key : 1 Comparative example  
 2 Comparative photosensitive material  
 3 Comparative pigment

It is understood from Tables 1 and 2 that the photosensitive materials of the present invention have high sensitivity.

#### Application Examples 6-10

The photosensitive materials of Application Examples 1-5 and Comparative Examples 1, 2 were applied to the cylinder of the electrophotographic copier provided with corona discharger, exposure optical system, developer, transfer charger, charge removing exposure optical system and cleaner. In this copier, images were obtained on transfer paper accompanied with driving of the cylinder. The initial light potential ( $V_L$ ) and dark potential ( $V_D$ ) in the copier were set to -200 V and -700 V, respectively, and the fluctuation amounts  $\Delta V_D$ ,  $\Delta V_L$  of light potential ( $V_L^{10000}$ ) and dark potential ( $V_D^{10000}$ ) after using 10,000 times were measured. The results are shown in Table 3. Furthermore, the negative symbol in  $\Delta V_D$  and  $\Delta V_L$  shows lowering of potential, and the positive symbol shows rising of potential.

Table 3

① 例	② 感光体 No.	$\Delta V_D$ (V)	$\Delta V_L$ (V)
③ 実施例 6	1	-6	+5
実施例 7	2	-5	0
実施例 8	3	-10	+7
実施例 9	4	+5	0
実施例 10	5	0	+5
④ 比較例 3	比較感光体 1	-50	+60
比較例 4	比較感光体 2 ⑤	-30	+50

Key: 1 Example  
 2 Photosensitive material  
 3 Application Example  
 4 Comparative Example  
 5 Comparative photosensitive material

It is seen from Table 3 that the fluctuation in potential in repeated used is low in the photosensitive materials obtained using the disazo pigments of the present invention.

#### Comparative Examples 5-11

Photosensitive materials were manufactured in the same manner as in Application Examples 1-5 except that a hydrazone compound having the structure shown below, instead of styryl compound (T-39) used in Application Examples 1-5 and Comparative Examples 1 and 2, was used, and their electrification characteristics were measured. In addition, the level potential fluctuation was measured in the same manner as in Application Examples 6-10. The results are shown in Table 4.

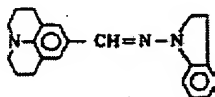


Table 4

① 比較例 No.	② 比較感光 体No.	③ アゾ染料 No.	$V_D$ (V)	$V_D$ (V)	E <sub>1/2</sub> (lux·sec)	$\Delta V_D$ (V)	$\Delta V_L$ (V)
5	3	G-13	-700	-630	1.70	-20	+15
6	4	G-10	-700	-640	2.73	-20	+5
7	5	G-11	-690	-650	3.99	-30	+20
8	6	G-14	-730	-660	3.20	-5	+15
9	7	G-19	-700	-640	1.51	-10	+20
10	1	比較染料1	-700	-560	10.5	-90	+80
11	2	比較染料2	-690	-500	6.25	-60	+100

Key: 1 Comparative Example  
 2 Photoreceptor No.  
 3 Azo pigment No.  
 4 Comparative compound

According to Table 4, photosensitive materials having excellent characteristics can be obtained by combining the styryl compound and disazo pigments of the present invention. Furthermore, it is seen that in the disazo pigments of the present invention, deterioration in characteristics is low even when the charge-transporting material is changed, and the selection range of the charge-transporting material is wide.

#### Application Example 11

The above-illustrated disazo pigment (G-45) 5 g was mixed with 100 mL of cyclohexanone and dispersed in a ball mill for 10 min. The dispersion was coated at a dry thickness of 0.5  $\mu\text{m}$  on an aluminum plate to form a carrier-generating layer. Then, 10 g of the above-illustrated charge-transporting material T-60 and 10 g of bisphenol A type polycarbonate resin (viscosity-average molecular weight: 28,000) were dissolved in 70 mL of 1,2-dichloroethane, and the solution was coated at a dry thickness of 18  $\mu\text{m}$  on the carrier-generating layer to form a carrier-transporting layer to obtain an electrophotographic photosensitive material of the present invention.

The electrophotographic characteristics of the photosensitive material thus obtained were measured. Furthermore, the same measurement was repeated 1000 times. Furthermore, the dispersion used in this application example was allowed to stand for 1 month, and a



photosensitive material was manufactured in the same manner as above and its electrophotographic characteristics were measured. The results are shown in Table 5.

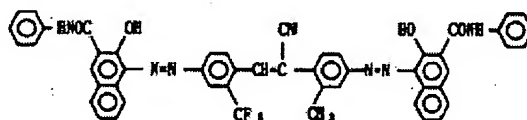
Table 5

	①		②		③	
	第1回目	第1000回目	分散液を1ヵ月放置後		第1回目	第1000回目
			第1回目	第1000回目		
$V_o$ (V)	-700	-696	-700	-696		
$V_d$ (V)	-680	-678	-681	-677		
$E\%$ (lux · sec)	1.9	1.9	1.9	1.9		

Key: 1 First time  
 2 At 100<sup>th</sup> time  
 3 After allowing dispersion to stand for 1 month

### Comparative Example 12

A comparative photosensitive material was manufactured in the same manner as in Application Example 11 using the following disazo pigment described in Japanese Kokai Patent Application Sho 59[1984]-7365 as the carrier-generating material.



The same measurement as that in Application Example 11 was conducted on this photosensitive material, and the results are shown in Table 6.

Table 6

	①		②		③	
	第1回目	第1000回目	分散液を1ヵ月放置後		第1回目	第1000回目
			第1回目	第1000回目		
$V_o$ (V)	-690	-600	-600	-540		
$V_d$ (V)	-650	-580	-590	-600		
$E\%$ (lux · sec)	2.5	2.6	4.0	4.1		

Key: 1 First time  
 2 100<sup>th</sup> time  
 3 After allowing dispersion to stand for 1 month

As is clear from the above results, the carrier-generating material of the comparative examples displays the characteristic even when the dispersing time is short, but the change in dispersion over time is significant, which becomes an obstacle in practical use. The electrophotographic photosensitive materials of the present invention can reveal sufficient characteristics even when the dispersing time is short, moreover the change in dispersion over time is almost negligible. Therefore they are superior in practical use.

#### Effect of the invention

The improvement of carrier generation efficiency and carrier transport efficiency in the photosensitive material is devised by a combination of disazo pigment and styryl compound according to the present invention and, as a result, electrophotographic photosensitive materials having high sensitivity and superior durability and potential stability can be obtained. In addition, the disazo pigments of the present invention have satisfactory stability in dispersed state and exhibit superior characteristics in practical use. Furthermore, the photosensitive materials of the present invention show high electrophotographic sensitivity in light emitting wavelength regions of LEDs by selecting substitution groups of the azo pigments.

#### Brief description of the figures

Figure 1 is a drawing showing schematically the layer constitution of an electrophotographic photosensitive material. Figures 2 and 3 show the spectral sensitivity of the application examples.

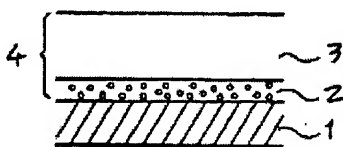


Figure 1

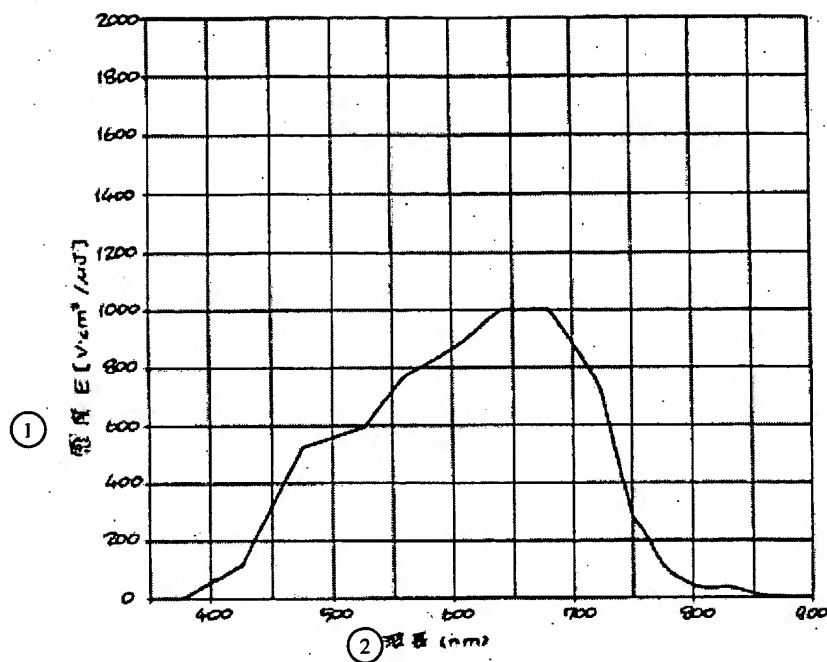


Figure 2

Key: 1 Sensitivity  $E$  ( $\text{V}\cdot\text{cm}^2/\mu\text{J}$ )  
 2 Wavelength (nm)

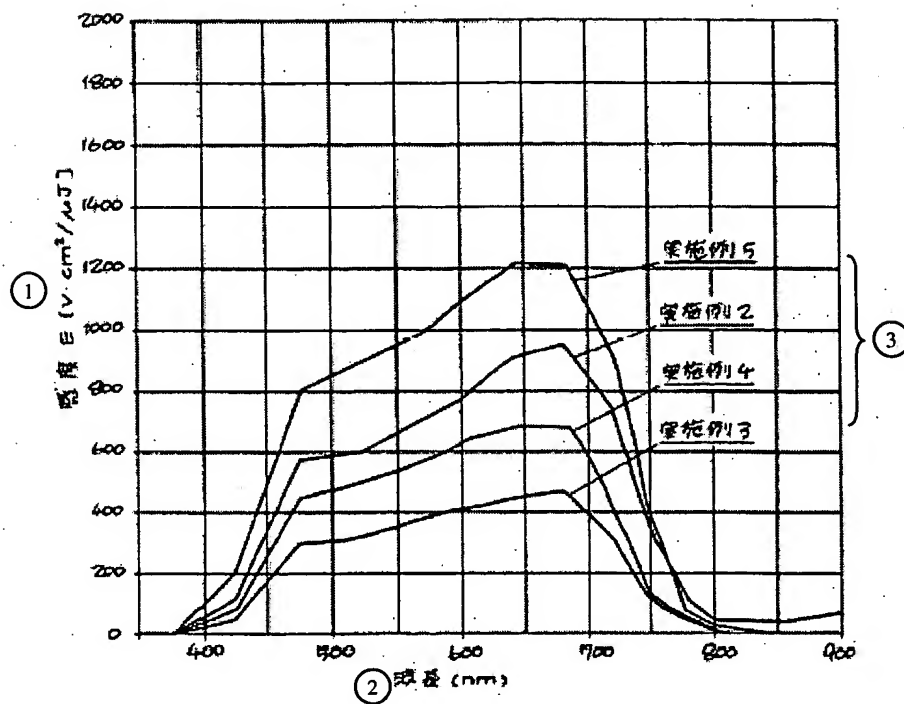


Figure 3

Key: 1 Sensitivity  $E$  [V.cm<sup>2</sup>/μJ]  
 2 Wavelength (nm)  
 3 Application Example \_\_\_\_\_

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